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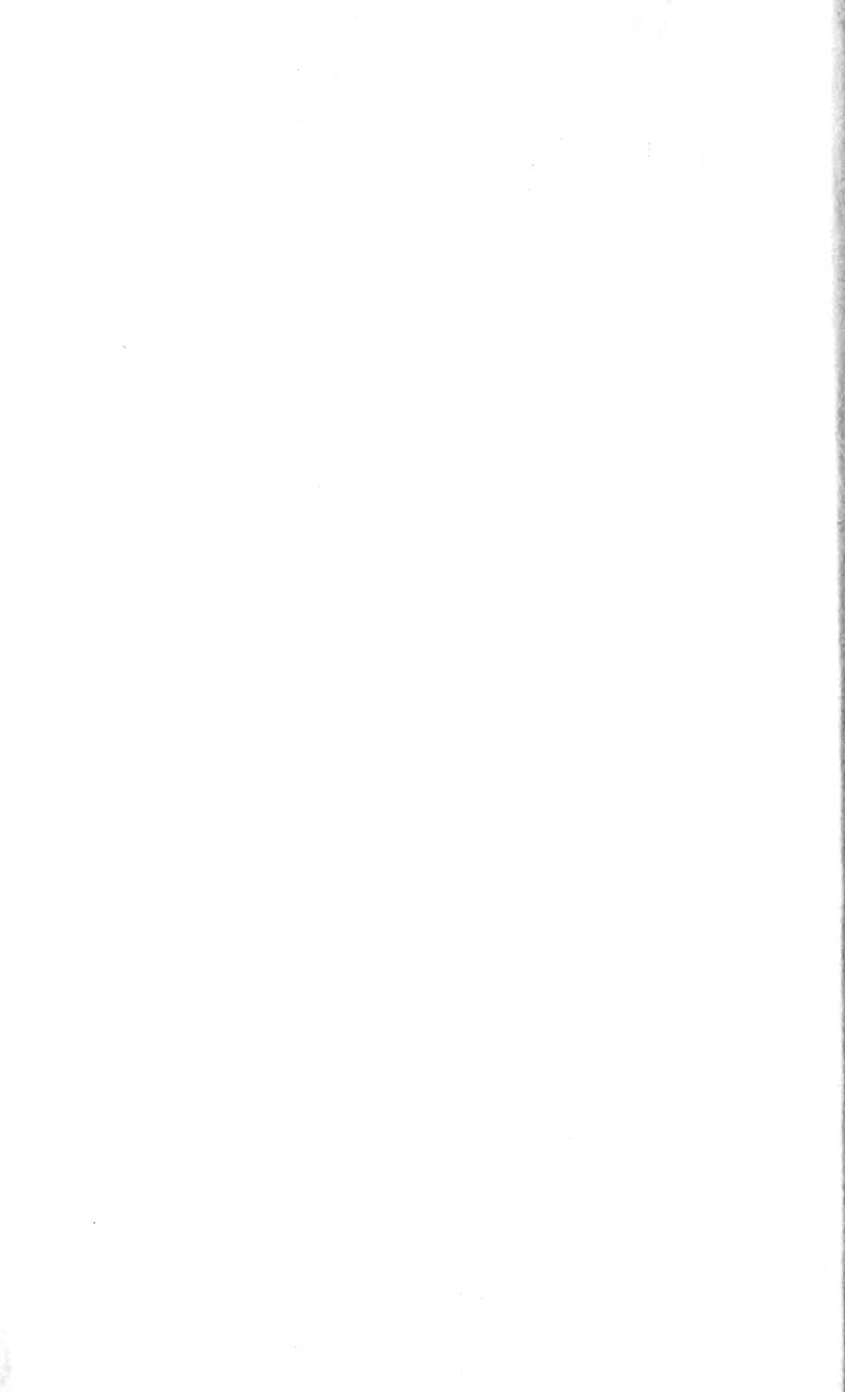
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SKETCH OF  
THERMODYNAMICS.

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SKETCH  
OF  
THERMODYNAMICS

BY  
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SECOND EDITION.  
(REVISED AND EXTENDED.)

EDINBURGH:  
DAVID DOUGLAS.

1877.



## P R E F A C E.

TWO considerations led to the first publication of this little work. Representations were made by various men of science, especially engineers, to the publishers of the *North British Review*, to the effect that it was desirable that two articles of mine, on the 'Dynamical Theory of Heat' and on 'Energy,' which appeared in that Journal in 1864, should be reprinted in a separate form. And I felt the want of a short and elementary text-book on these subjects, to be used in my class, until the publication of the volume of *Thomson and Tait's Natural Philosophy* in which they will be treated.

The semi-historical character of the articles has been retained, although it is to a certain extent unsuited for a text-book. Want of time, and the desire to republish them in a form not very different from the original one, have been my reasons.

I have added, for the benefit of the reader who has some knowledge of mathematics, developments of a somewhat more advanced character, mainly taken from the scattered papers of Sir W. Thomson.

The science of Thermodynamics is now securely founded upon bases almost as simply enunited, and quite as impregnable, as Newton's *Laws of Motion* ;

and the opposition which it even yet occasionally meets with is therefore quite as absurd as would be a denial of the main conclusions of the *Principia*.

Since the appearance of my articles in the *North British Review*, I have been led to examine very carefully the history of the subject, and have consequently made several alterations. Nevertheless, in attempting to give even a rough sketch of the history of a grand physical theory, especially one of so modern a date, I have been convinced by experience that it is almost impossible to be strictly impartial, however we may strive to be so.

Take an instance, or two. In almost all French and German works we read of the 'gaseous laws of Mariotte and Gay-Lussac.' British authors usually call them the laws of Boyle and Dalton. It is probable that both are wrong, the British partially, the French and Germans wholly. Boyle<sup>1</sup> discovered, and published several years before the earliest work of Mariotte<sup>2</sup> which I have been able to find, the law connecting the pressure and volume of a gas at constant temperature, employing for the purpose the

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<sup>1</sup> *Defence of the Doctrine touching the Spring and Weight of the Air, against the objections of Franciscus Linus*. Appended to *New Experiments, physico-mechanical, etc.* Second Edition, 4to. Oxford, 1662. See also James Bernoulli, 1683, *De Gravitate Ætheris*, p. 92, where he distinctly ascribes these experiments to Boyle.

<sup>2</sup> In the *Biographie Générale*, the date of the treatise *De la Nature de l'Air* is given as 1676. In the *Histoire de l'Académie*, 1666-86, and in the *Biographie Universelle*, the date appears as 1679. But Prof. Jenkin informs me that even the British Museum does not afford the means of determining the date exactly.

very apparatus still used in Physical lectures. And it was Charles<sup>1</sup> who discovered that the co-efficient of dilatation is nearly the same in all permanent gases. Their equable expansion for equal increments of temperature as measured by the mercury thermometer seems to have been quietly assumed, although it is by some stated to be the essence of the so-called Gay-Lussac Law. Dalton<sup>2</sup> states that 'air expands in geometrical progression to equal increments of temperature' as measured by a peculiar scale, which he says very nearly agrees with the common mercurial scale.

When errors like these are almost universal, where can we expect to find truth? Even so excellent an authority as the late M. Verdet, whose extensive knowledge and whose love of truth were equally conspicuous, made statements as to the history of Thermodynamics which he afterwards frankly acknowledged to be incorrect. The following, for instance, amongst others, was noticed in the *North British Review*; but one has only to look to the recently published volumes of his collected works to

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<sup>1</sup> Verdet—*Leçons de Chimie et de Physique*, 1862. Note E. See, however, Gay-Lussac himself: *Ann. de Chimie*, xliii. (An x.) p. 157. 'Avant d'aller plus loin, je dois prévenir que quoique j'eusse reconnu un grand nombre de fois que les gaz oxygène, azote, hydrogène, et acide carbonique, et l'air atmosphérique, se dilatent également depuis 0° jusqu'à 80°, le cit. Charles avait remarqué depuis 15 ans la même propriété dans ces gaz :—mais, n'ayant jamais publié ses résultats, c'est par le plus grand hasard que je les ai connus. . . . Il me paraît donc qu'on ne peut conclure de ces expériences la vraie dilatation des gaz.'

<sup>2</sup> *Chemical Philosophy*, 1808.

find a great many more. It is not fair to the memory of such a man to publish his lectures without at least indicating the corrections which death alone prevented him from making :—

‘À une somme donnée d’actions chimiques de nature donnée doit correspondre un dégagement constant de chaleur, quelle que soit la constitution de la pile et du circuit où les deux phénomènes se produisent à la fois. Cette conclusion théorique a été vérifiée par une remarquable expérience de M. Favre.’

This was no theoretical deduction at all, but an experimental result given by Joule in 1843 [see sect. 93 of this work] ; while the earliest of Favre’s experiments dates from 1853. I refer to it here as a good instance of the way in which the contents of Joule’s magnificent, but much neglected, papers of a quarter of a century ago are being rediscovered and attributed to others.

I cannot pretend to absolute accuracy, but I have taken every means of ensuring it, to the best of my ability ; though it is possible that circumstances may have led me to regard the question from a somewhat too British point of view. I have tried to preserve a happy medium between the old absurd British contempt for all things foreign, and the still more absurd custom (of comparatively recent origin) which gives to foreigners *all* that the writer is not in a position to claim for himself or for some of his particular friends. But, even supposing the worst, it appears to me that unless contemporary history be written with some

little partiality, it will be impossible for the future historian to compile from the works of the present day a complete and unbiassed statement. Are not both judge and jury greatly assisted to a correct verdict by the avowedly partial statements of rival pleaders? If not, where is the use of counsel?

But that I may show the reader that I am in no way prejudiced—though I have formed an opinion—I quote, from some critical remarks which Prof. Helmholtz has been kind enough to make on my introductory chapters, an admirable statement of a part at least of the case for the other side. It will be remembered that there is no dispute about dates, there is a difference of opinion as to the validity of processes, and the credit to be assigned to their authors.

‘ . . . ich<sup>1</sup> muss sagen, dass mir in dieser Beziehung die Entdeckungen von Kirchhoff in diesem Felde (*Radiation and Absorption*) als einer der lehrreichsten Fälle in der Geschichte der Wissenschaft erscheinen, eben auch deshalb weil viele andere Forscher schon vorher dicht am Rande derselben Entdeckungen gewesen waren. Kirchhoff's Vorgänger verhalten sich zu ihm in diesem Felde ungefähr so, wie in Bezug auf die Erhaltung der Kraft

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<sup>1</sup> Freely translated, it is as follows :—. . . I must say that, in this connection, Kirchhoff's discoveries about radiation and absorption appear to me one of the most instructive cases in the history of science ; and the more so that many other investigators had already approached close to the verge of these discoveries. Kirchhoff's predecessors in this field bore to him much the same relation as, in the Conservation

R. Mayer, Colding, und Séguin zu Joule und W. Thomson.

‘Was nun R. Mayer betrifft, so kann ich allerdings den Standpunct, den Sie ihm gegenüber eingenommen haben, begreifen, kann aber doch diese Gelegenheit nicht hingehen lassen, ohne auszusprechen, dass ich nicht ganz derselben Meinung bin. Der Fortschritt der Naturwissenschaften hängt davon ab, dass aus den vorhandenen Thatsachen immer neue Inductionen gebildet werden, und dass dann die Folgerungen dieser Inductionen, soweit sie sich auf neue Thatsachen beziehen, mit der Wirklichkeit durch das Experiment verglichen werden. Ueber die Nothwendigkeit dieses zweiten Geschäfts kann kein Zweifel sein. Es wird auch oft dieser zweite Theil einen grossen Aufwand von Arbeit und Scharfsinn kosten, und dem, der ihn gut durchführt, zum höchsten Verdienste gerechnet werden. Aber der Ruhm der Erfindung haftet doch an dem, der die neue Idee gefunden hat; die experimentelle Prüfung ist nach-

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of Energy, Mayer, Colding, and Séguin bore to Joule and W. Thomson.

As concerns Mayer, I can of course understand the point of view from which you regard him; but I cannot allow this opportunity to pass without saying that I am not quite of the same opinion. The progress of Natural Science depends upon the constant formation of new inductions from known facts, and the comparison of these inductions, so far as they lead to new consequences, with reality by means of experiment. There can be no doubt of the necessity of this second step. It often requires an extensive application both of labour and talent, and it brings the greatest credit to him who executes it well. But the glory of the discovery belongs to him who hits upon the new idea; the subsequent experimental verification is often a mere mechanical pro-



her offenbar eine viel mechanischere Art der Leistung. Auch kann man nicht unbedingt verlangen, dass der Erfinder der Idee nothwendig verpflichtet sei, auch den zweiten Theil der Arbeit auszuführen. Damit würden wir den grössten Theil der Arbeiten mathematischer Physiker verwerfen. Auch W. Thomson hat eine Reihe theoretischer Arbeiten über Carnot's Gesetz und dessen Consequenzen gemacht, ehe er ein einziges Experiment darüber anstellte, und keinem von uns wird einfallen, deshalb jene Arbeiten gering schätzen zu wollen.

‘R. Mayer war nicht in der Lage, Versuche anstellen zu können; er wurde von den ihm bekannten Physikern zurückgewiesen (noch mehrere Jahre später ging es mir ebenso), er konnte kaum Raum für die Veröffentlichung seiner ersten zusammengedrängten Darstellung gewinnen. Sie werden wissen, dass er in Folge dieser Zurückweisungen zuletzt geisteskrank wurde. Es ist jetzt schwer sich in den Gedanken-

---

cedure. And we must not unconditionally require that the discoverer of the idea should necessarily be bound to carry out the second part of the work. For we should thus have to reject the greater part of the work of mathematical physicists. Even W. Thomson published a series of theoretical investigations about Carnot's law and its consequences, before he had made a single experiment connected with it, and it would not occur to any of us to value these investigations lightly in consequence.

Mayer was not in a position to make experiments; he was repulsed by the physicists with whom he was acquainted (several years later I was similarly treated), and could scarcely procure room for the publication of his first compressed exposition. You must know that in consequence of these repulses his mind at last became affected. It is difficult now to transport oneself back into the circle of thought of that

kreis jener Zeit zurück zu versetzen und sich klar zu machen, wie absolut neu damals die Sache erschien. Mir scheint dass auch Joule lange hat um Anerkennung seiner Entdeckung kämpfen müssen.

‘Obgleich also niemand leugnen wird, dass Joule viel mehr gethan hat, als Mayer, und dass in des letzteren ersten Abhandlungen viele Einzelheiten unklar sind, so glaube ich doch, muss man Mayer als einen Mann betrachten, der unabhängig und selbständig diesen Gedanken gefunden hat, der den grössten neueren Fortschritt der Naturwissenschaft bedingte, und sein Verdienst wird jedenfalls dadurch nicht geringer, dass gleichzeitig ein Andrer in einem anderen Lande und Wirkungskreise dieselbe Entdeckung gemacht, und sie nachher freilich besser durchgeführt hat, als er.’

With a great part of this I cordially agree, and, had I to write these chapters afresh, I should probably advert less strongly than I have done to the defects and errors of Mayer’s earliest paper. But as my remarks have, for the most part, been already published, and as I am still convinced of their justice,

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time, and to perceive clearly how absolutely new the matter then appeared. It seems to me that even Joule had to struggle long for the recognition of his discovery.

Thus, although no one will deny that Joule has done far more than Mayer, and that in the early writings of the latter many points are not clear, I believe that Mayer must be considered as a man who independently and for himself discovered this thought which has produced the grandest recent advance of natural science; and his deserts are by no means diminished by the fact that, simultaneously, another, in another country and sphere of action, made the same discovery, and indeed has since developed it better than he.

I think it best to retain them, giving Mayer, however, the benefit of the able and weighty advocacy of Helmholtz. It will be seen, however, that those who with astonishing want of consistency, refuse Stokes and Stewart any credit as against Kirchhoff, while giving *all* to Mayer as against Joule, obtain no sympathy from such a man as Helmholtz.

There are, of course, many others besides Mayer, whose claims are here discussed. To some of these my statements may not be satisfactory. I can only say to such that, as I am not consciously unfair, I shall heartily acknowledge any misstatements regarding their claims which they may prove me to have made. But where an experimenter's claims are founded upon mere *verifications* of facts deduced from a theory already securely based upon other facts and therefore *certain*, I avoid as far as possible all notice of them. Such experimenters have claims resembling those of Falstaff to the death of Hotspur!

I have to express my gratitude to numerous friends, but especially to Professors Jenkin and Clerk-Maxwell, and the late Professor Rankine, to whose kind assistance the volume is largely indebted for accuracy and completeness. The subject is one of vast importance, but very few indeed are yet acquainted with even its most elementary facts; and by many of these it is not yet accepted as true. Besides, the developments which it has received during the last twenty-five years have to be sought for in scattered papers in the scientific journals or

the transactions of learned societies. I can but hope that I have made the student's progress easier by giving him a general sketch of it, with copious references to the works in which he will find farther information.

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Reasons similar to those which led to the publication of the first edition of this work appear to call for a second. Several books on Thermodynamics (and especially the very valuable treatise by Clerk-Maxwell) have appeared since 1868, but none that I have met with takes at all the same ground as this.

It has been carefully revised; in some places considerably modified, and in others extended. To have introduced results, like those of Andrews on the critical temperature of a gas, or of J. Thomson and Willard Gibbs on the triple point, etc., would have been impossible without greatly enlarging the volume. The semi-historical form of the work has rendered classification by divisions of the subject-matter impossible. I hope that the introduction of a Table of Contents, which Mr. Scott Lang has kindly drawn up for me, will remove any inconvenience arising from this cause.

Here my Preface might have ended, had not some remarks been made upon the first edition by a philosopher whose high scientific position requires that I should explain *why* I have not altered the passages objected to.

Having written the work in good faith, and after somewhat extensive reading; and having, in consequence of some objections made by Professor Clausius to my first article in the *North British Review*, been fortunate enough to induce the late Professor Macquorn Rankine to re-write for me the chief paragraphs dealing with Professor Clausius' work, I was somewhat surprised to find myself accused by the latter of misrepresentation.<sup>1</sup> In the new edition of his *Abhandlungen* recently published, Professor Clausius has modified this accusation to the charge that my book was written with the view of claiming the Dynamical Theory of Heat as far as possible for the British nation. He adds that he can bring forward the most definite grounds for this opinion. As such a purpose never occurred to me, I have anxiously tried to find what portions of my book can be considered open to such a charge. The result of my inquiries is not likely to be satisfactory to Professor Clausius, for I have now, after careful revision of the whole documentary evidence, found it necessary to cancel certain additions which I had made to the paragraphs written for me by Rankine. These paragraphs, I now see, were correct as they originally stood. But, thinking them too severe on Professor Clausius' claims, I rashly added some mitigating passages, which I have now

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<sup>1</sup> The correspondence will be found at full length in the *Philosophical Magazine*, 1872, and it will be seen that Professor Clausius fancies himself to have received even worse treatment from Clerk-Maxwell than from myself. The first only of my letters was sent to *Poggendorff's Annalen*.

been obliged to retract as unsupported by evidence. This part of Professor Clausius' attack was, therefore, really directed against Rankine's statements, although I had (unjustifiably as I now see) softened them down before publishing them.

Professor Clausius adds that my book is *sehr geschickt abgefasst*. Read by the light of the context this can only mean that it is skilled special pleading. It is curious to see how complex and artful one may be considered who keeps ingenuously to facts.

Professor Clausius also says that the expression

$$t_0 \int \frac{dq}{t}$$

(§ 178, below) is his own, and that in claiming it for Sir W. Thomson I referred to an article (*On a Universal Tendency in Nature to the Dissipation of Mechanical Energy. Phil. Mag.*, vol. iv., 1852) 'in which neither that expression nor any expression of like meaning can be found.' This is very strange indeed. Professor Clausius ought to have seen at once that the problems proposed and solved in that article of Thomson's *must* have involved in their solution the expression in question—even if formulæ had not been given. Thomson distinctly states in the article the conditions under which energy is dissipated. In connection with one of his statements he solves an important problem connected with the œconomic working of a steam-engine, and gives the expression

$$Rw \text{ or } w\epsilon^{-\frac{1}{J} \int_T^S \mu dt}$$

for the portion, of the heat  $w$ , which is 'absolutely and irrecoverably wasted.' The whole matter is contained in this. At the time of publication of that article, Thomson and Joule were engaged in the necessary work of trying *by experiment* whether

$$t = \frac{J}{\mu} - a$$

(another of the formulæ in the article) agreed sufficiently with the ordinary air-thermometer reckoning of temperature to be a convenient assumption. With this, the above expression for the waste becomes

$$(T+a) \frac{w}{S+a},$$

or (in my notation, § 178)

$$t_0 \frac{dq}{t}.$$

There are obvious misprints in the other formulæ of the article (which are corrected in the list of *Errata* in the *next* volume of the *Phil. Mag.*), but these do not affect the meaning of the dissipation, nor the expression given for it—which is merely the integral of that last written.

In *Pogg. Ann.*, Heft 9., 1877, which I have just seen, Professor Clausius attacks the Demon-theory of Clerk-Maxwell, as applied in my *Recent Advances in Physical Science* to show the inconclusiveness of his attempt to establish the second Law of Thermo-

dynamics. Professor Clausius says he has not seen Clerk-Maxwell's own statement of his theory ; which is strange, inasmuch as it is contained in that very work of Clerk-Maxwell's<sup>1</sup> of which he so strongly complained in 1872. In his quotations he altogether ignores the chief point urged against him in my *Lectures*, viz., that what demons could do on a large scale really goes on without the help of demons (though on a very small scale) in every mass of gas—that is, of course, if the kinetic theory of gaseous pressure be true. [See the text below, § 53.] For this reason, and also because Professor Clausius announces that he has not yet completed his statements, I do not think it necessary for the present to say more on this subject.

But this discussion has brought to my recollection a paper read by Sir W. Thomson to the Royal Society of Edinburgh, on the *Kinetic Theory of the Dissipation of Energy*.<sup>2</sup> Had I thought of this paper in time, I should have inserted some valuable extracts from it in the present edition.

P. G. TAIT.

COLLEGE, EDINBURGH, *November 1877.*

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<sup>1</sup> *Theory of Heat*, 1st ed. 1871, p. 308; 4th ed. 1875, p. 328.

<sup>2</sup> *Proc. R.S.E.*, or *Nature*, April 1874.



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## CHAPTER I.

### HISTORICAL SKETCH OF THE DYNAMICAL THEORY OF HEAT.

1. *What is Heat?*—The metaphysical arguments on this question, which, in countless heaps, encumber the shelves of mediæval libraries, would merely stupify the reader, and tend to prevent him from easily understanding the actual facts, and their bearings. From the earliest times man's apprehension of the causes and connections of natural phenomena has been rendered uncertain and imperfect by his wilfully ignoring the great fact that Natural Philosophy is an *experimental*, and not an *intuitive*, science. No *à priori* reasoning can conduct us demonstratively to a single physical truth; we must endeavour to discover what *is*, not speculate on what might have been, or presumptuously decide what ought to have been. Hence it matters not to us what Aristotle or Bacon may have laid down, or Locke and Descartes imagined, with regard to the nature of heat.

2. It would be of little use to waste time in a preliminary sketch of the early history of our subject. Such a sketch might, perhaps, be made very attractive, but the materials for it do not yet appear to have been collected. The rapid march of modern discovery renders it not only useless, but destructive, to the progress of the Natural Philosopher to spend much time or trouble in exploring the beginnings of his science. While he gropes about, seeking the source, his contemporaries are borne, with ever-increasing swiftness, along the broadening and deepening current of the river, to the 'great ocean of truth which lies unexplored before them.'

3. In the physical world we are cognisant of but four elementary ideas besides the inevitable *Time* and *Space*. They are *Matter*, *Force*, *Position*, and *Motion*; and *Matter* is said to possess *Energy* in virtue of its position or its motion. Of these, motion is merely change of position; and every change of motion of matter is commonly said to be due to force. In reality force is merely the rate at which energy is transferred or transformed per unit of length in a given direction, or the rate at which it would be transferred or transformed if some obstacle were removed. The notion of force is directly suggested to us by our so-called 'muscular sense'—and it is thus difficult to get rid of the idea that there is such a *thing* as force. But the direct evidence of our senses, uninterpreted by reason, is usually wholly misleading, when not meaningless, in physical science. Now it is evident that to one or other of the four elementary ideas above every distinct physical conception must be referred. To which does heat belong? The old notions of heat were that it was *Matter*; or, according to some Philosophers, *Force*. It is only within about a century that proofs have been gradually arrived at that when a body is hot its particles are in *Motion*; and that the so-called 'Latent Heat' of Black may possibly not be heat at all, but may depend on *Position*; in other words, that heat is in all cases a form of *Energy*. These may be startling statements, as they are now advanced, but they will be fully explained, and to some extent developed, in the course of the work.

4. Thus it appears that, of the four available hypotheses as to the nature of Heat, the *two necessarily erroneous* ones have, till lately, been almost universally adopted. So much for the trustworthiness of the metaphysical treatment of a physical question! Such a lesson should never be lost sight of; so deserved and so complete a refutation of the sophistical nonsense of the schoolmen, and so valuable a warning to the 'Philosopher' who may be disposed to *à priori* argument as

more dignified and less laborious than experiment, can scarcely occur again. Even the despised perpetual-motionist has more reason on his side than the metaphysical pretender to discovery of the laws of nature ; he, to his cost—but to his credit also—appeals to experiment to test the validity of his principle ; but the mighty intellect of his rival scorns such peddling with apparatus, to *it* all truth is intuitive ; nay more, what *it* cannot comprehend cannot be truth. But the days of its authority have nearly expired—happily for human progress.

5. When heat was considered to be matter, under the name of *Caloric*, it was of course regarded as uncreatable and indestructible by any process at the command of man. And there can be no doubt that many very plausible explanations of curious physical phenomena were arrived at by the labour and ingenuity of the partisans of this theory. Thus it was natural to suppose that, when caloric entered a body, or rather combined with it, the body should in general expand ; and, even when heating produced contraction, there were analogies, quite sufficient to bear out the theory, supplied by such mixtures as alcohol and water, or alloys as copper and tin ; where the bulk of the compound is considerably less than the sum of the bulks of the components : and, as Faraday has shown in the combination of potassium and oxygen, sometimes less than the bulk of either. Conduction of heat, or transference of caloric from one body to another, or from part to part of the same body, also presented no difficulty. So it was with the experiments which led to what was called (from the principles of this theory) the *Specific Heat* of bodies ; it had merely to be assumed that different bodies required different proportions of caloric to be mixed with them to produce equal effects in the form of change of temperature. Thus, the specific heat of water being called 1, that of mercury is  $\cdot 033$ , *i.e.* a pound of water requires 30 times more caloric to be mixed with it to produce a given change of temperature (measured by the

thermometer) than a pound of mercury. The fact that in heating ice no rise of temperature is observed, however much heat may have been applied, until the whole of the ice is melted—and similar phenomena observed in every case of melting or liquefaction, as well as in boiling or vaporization—led Black to propound the doctrine of *Latent Heat*. The fundamental ideas of this doctrine, that water differs from ice at the same temperature simply by the admixture of a definite equivalent of caloric ; that the steam which escapes from boiling water, though showing the same temperature when tested by the thermometer, contains a vastly greater amount of caloric ; and similar ideas for all similar cases, were thus easily and directly reduced to the caloric theory. The additional quantity of caloric was supposed simply to change the molecular state of the body, without altering its temperature : hence it was said to be *latent*. There need be no hesitation, so far as these, and many other, phenomena of heat are concerned, in pronouncing the explanations given by the material theory quite satisfactory, although in several cases they are certainly cumbrous, and difficult of application. The following extract from Black's *Lectures*<sup>1</sup> gives a very fair idea of some of the best of these speculations and attempts at explanation :—

‘ Thus, to consider in the first place, the slaking of lime, the formation of lime-water, and some of the qualities of lime-water : The calcareous earth, in its quicklime state, or deprived of its air, as it has an attraction for water, will be found to resemble the salts in several particulars in the mode of this attraction. The salts, if we take them in their purest state, are disposed to combine with water in two different ways—with a certain quantity of water they unite closely, and with considerable force to constitute the crystals of salts—in which the water is joined with the particles of salt in such a manner as to become solid along with them. There are some of the salts which become very hot in uniting with this portion of water : such are Glauber's salt, Epsom salt, fixed alkali, and several others. This heat is supposed by most authors to come out of the salts ; I am rather inclined to think it comes from the water. After this, if more water be added, the salt unites

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<sup>1</sup> Edinburgh, 1803. Vol. ii. p. 73.

with it in a different manner, so as to become fluid along with it, or form a solution, or liquid, in which the salt is dissolved in the water ; and, in this part of the process, cold is produced. In the same manner, if water be added to quicklime, a certain quantity of it is attracted by the quicklime, and deprived of its fluidity with violence and heat ; and it adheres to the lime with considerable force, constituting with it a dry powder, which is called slaked lime. But if this slaked lime be mixed with a much larger quantity of water, a part of it is dissolved and composes with the water a lime-water.

‘The heat produced in slaking lime is just one of the numberless examples of the emersion of latent heat. And if any person should think that the heat produced in some of these instances is too great to be explained in this way, let him consider that the 140 degrees, which escape from water in congelation, refers only to the difference between the heats necessary for appearing in the forms of water and ice ; but we have no authority to say that the same abstraction of heat from the same quantity of water will suit its subsequent appearance in a crystal of Glauber’s salt, Epsom salt, or nitre. A much greater emersion may be necessary or a much less ; therefore, till the experiment be tried, we cannot say how much heat must emerge before the water can unite with quicklime in a solid form. And, let it be further remarked, that the heat extricated in this crystallization can be very little diminished by the subsequent solution, because there is very little lime dissolved in the lime-water.’

6. But another class of common phenomena afforded no such easy application of the theory—namely, the development of heat by friction or percussion ; and it must be allowed that many of the warmest supporters of the caloric hypothesis frankly admitted that their explanations of these effects were not quite satisfactory. The general tendency of these explanations was towards assuming a change in the capacity for caloric to be produced by the disintegration caused by friction or by the compression caused by impact—though it was excessively difficult to see how two such opposite processes could *each* produce a *diminution* of the capacity. And although the difficulty is lessened by considering a change in latent heat as well as in capacity to be produced by attrition or condensation, it is by no means removed.

7. The mischievous consequences of long persistence in a false theory were perhaps never better exemplified than in the case of this supposed materiality of heat ; for so completely were the scientific men of last century imbued with it, that when Davy gave a conclusive proof of the *actual creation of heat* in a very simple experiment, his consequent argument against the materiality of heat (or the existence of caloric) attracted little attention, and was treated by many of those who condescended to notice it as a wild and extravagant speculation. It is certain that even Davy himself was led astray in his argument, by using the hypothesis of change of capacity as the basis of his reasoning, and that he might have been met successfully by any able Calorist who, though maintaining the materiality of heat, might have been willing to throw overboard one or two of the less essential tenets of his school of philosophers.

8. But Davy's experiment, rightly viewed, is completely decisive of the question ; and, in spite of the imperfection of his reasoning from it (due entirely to the prevailing sophisms of the Calorists), was perfectly satisfactory to himself. He developed, in a singularly brief and lucid form, the fundamental principles of the true theory, in a tract, forming part of the *Contributions to Physical and Medical Knowledge, principally from the West of England, collected by Thomas Beddoes, M.D.*, published at Bristol in 1799.

9. Davy commenced by causing two pieces of ice to rub against each other, until both were almost entirely melted by the friction. Here water somewhat above the freezing point was produced. Davy's confused argument from this is as follows :—'From this experiment it is evident that ice by friction is converted into water, and according to the supposition its capacity is diminished ; but it is a well-known fact that the capacity of water for heat is much greater than that of ice ; and ice must have an absolute quantity of heat added to it before it can be converted into water. Friction, consequently, does not diminish the capacities of bodies for



heat.' To show that no heat was abstracted from surrounding bodies, he proceeded to cause two pieces of metal to rub against each other by means of clockwork, the whole apparatus being placed on a block of ice, which had some unfrozen water in a canal on its surface, and enclosed in a very perfect vacuum, produced by the now well-known application of carbonic acid gas and caustic potash. Here again heat was developed by the friction, but it did not come from the ice (for the water in contact with it was not frozen), nor from surrounding bodies (for in this case it must have passed through, and melted, the ice, but the ice remained unaltered). From these perfectly conclusive experiments, Davy proceeds thus:—

'Heat, then, or that power which prevents the actual contact of the corpuscles of bodies, and which is the cause of our peculiar sensations of heat and cold, may be defined a peculiar motion, probably a vibration, of the corpuscles of bodies, tending to separate them. It may with propriety be called the repulsive motion.'

'Bodies exist in different states, and these states depend on the differences of the action of attraction, and of the repulsive power, on their corpuscles, or, in other words, on their different quantities of attraction and repulsion.'

10. Let us here remark, incidentally, what an immense simplification is at once introduced into our conception of the laws which regulate the intermolecular forces in bodies. Davy, by a single sentence or two, thus demolished for ever the ingeniously unnatural speculations of Boscovich and his school, who represented the law of the force exerted by one molecule or particle of a body on another, by a most complex alternation of attractions and repulsions, succeeding each other as the distance between the two was gradually diminished, a law so inconsistent with the simplicity of that of gravitation, that it is amazing that it was ever seriously propounded.

11. Davy, in fact, makes this very application, and illustrates the effect of the repulsive motion in balancing the attraction of cohesion in bodies by the very apt comparison

to that of the orbital motion of a planet which prevents its being drawn nearer to the sun. We shall not attempt to follow his further development of this discovery, where he falls into an ingenious mistake in consequence of his belief in the corpuscular theory of light. It has nothing to do with our subject; yet, though now known to be erroneous, it is worthy of its author.

12. The rest of this short tract, so far as it relates to heat, is concerned with the laws of communication of heat, which are shown to be quite analogous to those of the communication of motion. It was not, however, so far as we know, till 1812 that Davy distinctly laid down, in a thoroughly comprehensive form, the law of the phenomenon. In his *Chemical Philosophy*, published in that year, he enuntiates the following perfectly definite and most important proposition:—

*‘The immediate cause of the phenomenon of heat, then, is motion, and the laws of its communication are precisely the same as the laws of the communication of motion.’*

The immense consequences of this statement we shall presently consider, after we have briefly described the labours of a contemporary of Davy, who *almost* succeeded, in 1798, in demonstrating the immateriality of heat; but whose work is especially valuable as containing the first recorded approximation to the measurement of heat in terms of ordinary mechanical units, which, singularly enough, does not appear to have been attempted by Davy.

13. In the *Philosophical Transactions* for 1798, there is a most instructive paper by Count Rumford,<sup>1</sup> entitled *An*

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<sup>1</sup> This remarkable man (Benjamin Thompson) was driven to Europe (for his loyalty) when the British colonies in America rebelled. He effected various important reforms in Bavaria, and chose the title by which he was generally known, and which was conferred on him for these services, from the village (now called *Concord*) in New Hampshire, where he had been obliged to leave his wife and his infant daughter.—*Biographie Générale*. See also *Memoir* by Ellis, 1876.

*Inquiry concerning the Source of the Heat which is excited by Friction.* The author's experiments were made at Munich while he superintended the boring of cannon in the Arsenal ; indeed, he remarks, that 'very interesting philosophical experiments may often be made, almost without trouble or expense, by means of machinery contrived for the mere mechanical purposes of the arts and manufactures.' He was struck with the very great heat developed by the friction or attrition of the steel borer on the brass casting ; and especially, in comparing it with the very small quantity of chips or powder removed from the metal, justly observing that it was inconceivable that a mere *change* of the capacity for heat in so small a relative quantity of brass could develop heat sufficient in some cases to *boil* a large quantity of water.

'In reasoning on this subject,' he says, 'we must not forget to consider that most remarkable circumstance, that the source of the heat generated by friction in these experiments appeared evidently to be *inexhaustible*.'

'It is hardly necessary to add that anything which any *insulated* body, or system of bodies, can continue to furnish *without limitation*, cannot possibly be a *material substance*, and it appears to me to be extremely difficult, if not quite impossible, to form any distinct idea of anything capable of being excited and communicated in the manner that heat was excited and communicated in these experiments, except it be MOTION.'

Had Rumford only completed his experiment, by dissolving separately in an acid the brass turnings, and an equal weight of the metal in large fragments, he would have been entitled to the sole credit of the experimental discovery of the true nature of heat.

We shall have occasion again to allude to the contents of this extremely lucid and philosophical paper ; meanwhile we may merely observe, that Rumford pointed out other methods to be employed in determining the amount of heat produced by the expenditure of mechanical power,

instancing particularly the agitation of water or other liquids, as in churning.

14. It may be well to pause for a moment at this stage, and carefully consider to what extent the true theory of heat had really been advanced about the commencement of the present century. And it is easy to see from the preceding pages that the following important facts were then completely acquired to science :—

- I. That Heat is Motion (or rather, in strict modern phraseology, Energy).
- II. That the laws of its communication are the same as those of the communication of Motion (or, in modern and more expressive phraseology, Energy).
- III. Hence that the laws of the communication of Heat are those laid down by Newton with such expressive brevity in the Scholium to his Third Law of Motion.
- IV. Hence that Heat has a definite mechanical value, and may be converted into mechanical effect, and *vice versâ*.
- V. That the determination of the accurate value of the mechanical equivalent of a given amount of heat, is a question to be resolved by experiment.
- VI. That Rumford had obtained an approximation (a pretty close one as we now know) to the value of this equivalent.
- VII. That this equivalent may be determined by expending work in the boring or friction of solids, or in agitating liquids.

15. For the benefit of such readers as may not be acquainted with the elements of mechanics, it will be useful to give a few explanations of some of the preceding statements, especially with the view of showing their logical sequence. I. and II. are simply Davy's own expression of his experimental conclusion. As to III. Newton shows, though not in precisely the same words, that when work is

expended solely in setting a body in motion, the *energy* of the motion is the measure of the work expended. This grand statement of Newton's will be considered in the next chapter. Work is here used in the ordinary engineering sense of so many 'foot-pounds,' *i.e.* so many pounds raised one foot. From this it follows that the heat present in a body is really a certain definite amount of energy of motion, which is equivalent to a certain definite amount of mechanical effect or work. This is statement IV. With reference to VI., which is the only other requiring explanation, it is easily calculated from the data of one of Rumford's experiments (*viz.*, that the work of one horse for 2h. 30m. raised, by 180° Fahr., the temperature of a mass equivalent in capacity for heat to 26·58 lbs. of water), that it requires about 940 foot-pounds of work to be expended to raise the temperature of a pound of water 1° Fahr. [We have somewhat altered the result first deduced by Joule from this experiment; for we have used 30,000 instead of 33,000 foot-pounds per minute as the value of a horse-power—the latter, or Watt's estimate, being now allowed to be too great.] No account was taken of the heat lost by radiation and evaporation, which must have been considerable from the high temperature produced, and the duration of the experiment; so that, as Rumford himself noticed, this value must be too high. It is now known to be about 20 per cent. too great; still it is a most remarkable result.

16. It does not follow that, if the chief fundamental laws and principles of a science are known, the *development* of them is an easy matter. Take, for instance, the law of gravitation. It is scarcely possible to conceive a simpler expression than this for the mutual action of two particles; yet, even for the simplest possible application, the motion of one *particle* about another, the numerical details are very troublesome; and when we have three mutually attracting particles, the problem (so far as *exact* solution is concerned) completely transcends the power of known mathematical

processes. It is, of course, infinitely more formidable when we consider the mutual action of the particles of a body ; and without the aid of hypotheses, suggested by experiment, such a case would be incapable of even *approximate* treatment. Thus we are prepared to find that for the practical application of the above facts regarding heat, hypotheses (of a kind suggested by experiment) will always be required until we know the mechanical constitution of bodies, and have immensely improved our mathematical methods.

17. For a considerable portion of the present century, Davy's discoveries about heat were neglected, or only casually mentioned ; but this was of comparatively little consequence, as their early reception might have kept back for a time the grand developments which must next be mentioned—immense strides in the theoretical and mathematical treatment of the subject, and to a considerable extent independent of the nature of heat. These are due to Fourier and Sadi Carnot, and it may well be said that it is in great part attributable to their remarkable works that the true theory of heat, when revived about thirty-five years ago, received so rapidly its present enormous development.

18. Fourier's *Théorie de la Chaleur*, composed before 1812, is one of the most exquisite mathematical works ever written, abounding in novel processes of the highest originality as well as practical utility. It is devoted solely (so far as its physical applications are concerned) to the problems of the *Conduction* and *Radiation* of heat. Whatever may eventually be found to be the true laws of conduction and radiation, Fourier gives the means of completely solving any problem involving these processes only, and applies his methods to various cases of the highest interest. He works out in detail these important cases with the particular assumption that the flux of heat is proportional to the rate at which the temperature changes along the line of flow ; and to a coefficient, depending on the nature of the body, called its *Conductivity*. It is only very recently indeed

that Forbes<sup>1</sup> has shown that the conductivity of a body for heat diminishes as its temperature increases ; and thus that the *details* of Fourier's solutions (in which the conductivity is assumed to be constant) are not strictly accurate when great differences of temperature are involved. But, besides the fact that Fourier has shown how to adapt his methods to *any* experimental data, the solutions he has given are approximate enough for application to many most interesting investigations, such as the secular cooling of the earth, underground temperature as depending on solar radiation, etc. By this powerful method, Fourier has reduced the treatment of any question involving transference of heat by conduction or radiation to a perfectly definite form ; and he must therefore stand, in the history of the subject, as one of its greatest promoters.

19. Very different in form and object from the systematic treatise of Fourier, is the profound and valuable essay of Sadi Carnot, *Reflexions sur la Puissance Motrice du Feu*, published in 1824.<sup>2</sup> The author endeavours to determine *how* it is that heat produces mechanical effect, and though some of his assumptions are not correct, he investigates the question in an exceedingly able and instructive manner. Starting with a correct principle, which, obvious as it is, has been sadly neglected by many later writers, he is led into error by assuming the materiality of heat. But with true philosophical caution he avoids committing himself to this hypothesis, though he makes it the foundation of his attempt to discover *how* work is produced from heat. He says :—

‘ If a body, after having experienced a certain number of transformations, be brought identically to its primitive physical state as to density, temperature, and molecular constitution, it must contain the same quantity of heat as that which it initially possessed ; or, in other words,

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<sup>1</sup> *British Association Report*, 1852. *Trans. R.S.E.* 1862-5.

<sup>2</sup> *An Account of Carnot's Theory of the Motive Power of Heat*, etc. by W. Thomson. *Trans. R.S.E.* 1849.

the quantities of heat lost by the body under one set of operations are precisely compensated by those which are absorbed in the others. This fact has never been doubted ; it has at first been admitted without reflection, and afterwards verified in many cases, by calorimetical experiments. To deny it would be to overturn the whole theory of heat, in which it is the fundamental principle. It must be admitted, however, that the chief foundations on which the theory of heat rests would require a most attentive examination. Several experimental facts appear nearly inexplicable in the actual state of this theory.'

This fundamental principle of Carnot is evidently axiomatic (so far as regards the quantity of heat in the body when it is restored to its original state): but there is a serious error as regards the equality of the quantities of heat received and given out by the body during the transformations.

20. The erroneous portion of the above statement of Carnot is contained in the clause, 'in other words, the quantities of heat lost by the body under one set of operations are precisely compensated by those which are absorbed in the others.' This is only true when as much work has been expended, in bringing back the body to its primitive state, as has been done by it in expanding. But we must remark the peculiar merit of Carnot's reasoning, which consists in the idea of bringing the body back to its initial state, as to temperature, density, and molecular condition, after a cycle of operations, before making any assertion as to the amount of heat which it contains. We shall be enabled to appreciate the value of this idea better when we see what others have been led to by ignoring it.

21. Thus, from Carnot's point of view, it is evident that the motive power of heat depends upon its being transferred from one body to another *through* the medium by whose change of volume or form the external mechanical effect is produced, as this medium is supposed to remain at the end of the operation in precisely the same state as at the commencement. He gives, as analogous, the instance of work derived from water falling from a higher to a lower level.



Hence, for the production of mechanical effect, we are to look to the successive communication of heat to, and abstraction of heat from, the particular medium employed ; and to illustrate this it is natural to consider the steam-engine as the most extensive practical application of the principle.

22. Carnot's reasoning may easily be made intelligible without mathematical details. In the simple case given below, all that is attempted is to show that in the ascent of the piston in the cylinder, *more* work is done against external forces than is required to be done by them to produce the descent and restore the piston to its first position. And in order that Carnot's axiom may be applied with strictness, and yet with simplicity, it is better to consider a hypothetical, than the actual, engine.

23. Suppose we have two bodies, *A* and *B*, whose temperatures, *S* and *T*, are maintained uniform, *A* being the warmer body, and suppose we have a stand, *C*, which is a non-conductor of heat. Let the piston and the sides of the cylinder be also non-conductors, but let the bottom of the cylinder be a perfect conductor ; and let the cylinder contain a little water, nearly touching the piston when pushed down. Set the cylinder on *A* ; then the water will at once acquire the temperature *S*, and steam at the same temperature will be formed till the space above the water is saturated, so that pressure must be exerted to prevent the piston from rising. Let us take this condition as our starting-point for the cycle of operations.

*First*, Allow the piston to rise gradually ; work is done by the pressure of the steam which goes on increasing in quantity as the piston rises, so as always to be at the same temperature and pressure. And *heat is abstracted from A*, namely, the latent heat of the steam formed during the operation.

*Second*, Place the cylinder on *C*, and allow the steam to raise the piston farther. More work is done, more steam is formed, but the temperature sinks on account of the latent

heat required for the formation of the new steam. Allow this process to go on till the temperature falls to  $T$ , the temperature of the body  $B$ .

*Third*, Now place the cylinder on  $B$ ; there is of course no transfer of heat. But if we now press down the piston, we do work upon the contents of the cylinder, steam is liquefied, and the latent heat developed is at once absorbed by  $B$ . Carry on this process *till the amount of heat given to  $B$  is exactly equal to that taken from  $A$*  in the first operation, and place the cylinder on the non-conductor  $C$ . The temperature of the contents is now  $T$ , and the amount of caloric in them is precisely the same as before the first operation.

*Fourth*, Press down the piston farther, till it occupies the same position as before the first operation; additional work is done on the contents of the cylinder, a farther amount of steam is liquefied, and the temperature rises.

Moreover, *it rises to  $S$  exactly*, by the fundamental axiom, because the volume occupied by the water and steam is the same as before the first operation, and the quantity of caloric they contain is also the same—as much having been abstracted in the third operation as was communicated in the first—while in the second and fourth operations the contents of the cylinder neither gain nor lose caloric, as they are surrounded by non-conductors.

Now, during the first two operations, work was done by the steam on the piston, during the last two work was done against the steam; on the whole, the work done by the steam exceeds that done upon it, since evidently the temperature of the contents, for any position of the piston in its ascent, was greater than for the same position in the descent, except at the initial and final positions, where it is the same. Hence the pressure also was greater at each stage in the ascent than at the corresponding stage in the descent, from which the theorem is evident.

Hence, on the whole, a certain amount of work has been communicated by the motion of the piston to external

bodies; and, the contents of the cylinder having been restored exactly to their primitive condition, we are entitled to regard this work as due to the caloric employed in the process. This we see was taken from *A* and wholly transferred to *B*. It thus appears that *caloric does work by being let down from a higher to a lower temperature*. And the reader may easily see that if we knew the laws which connect the pressure of saturated steam, and the amount of caloric it contains, with its volume and temperature, it would be possible to apply a rigorous calculation to the various processes of the cycle above explained, and to express by formulæ the amount of work gained on the whole in the series of operations, in terms of the temperatures (*S* and *T*) of the boiler and condenser of a steam-engine, and the whole amount of caloric which passes from one to the other.

24. Though the above process is exceedingly ingenious and important; it is to a considerable extent vitiated by the assumption of the materiality of heat which is made throughout. To show this, it is only necessary to consider the definition given for the limit to which the condensation is to be carried in the third operation; being that as much heat is to be emitted during it as was taken in during the first operation. But it is quite easy, as seems to have been first remarked by J. Thomson in 1849, to put Carnot's statement in a form which is rigorously correct, whatever be the nature of heat. J. Thomson says—

‘We should not say, in the third operation, “compress till the same amount of heat is given out as was taken in during the first.” But we should say, “compress till we have let out so much heat that the farther compression (during the fourth stage) to the original volume may give back the original temperature.”’

It is preferable, therefore, to go through Carnot's cycle again with the slight change of starting with the fourth of the preceding operations. This we leave to the student.

The reason will be easily apprehended by him when he reads the remarks on Watt's *Indicator Diagram* given in the third chapter.

It is but bare justice, however, to acknowledge that Carnot himself was by no means satisfied with the caloric hypothesis, and that he insinuates, as we have already seen, more than a mere suspicion of its correctness. The student may easily see the difficulty, if he considers that heat may be let down (by conduction merely) between bodies of different temperatures, without doing any work.

25. But we owe to Carnot much more than this, as will now be shown; deferring to a later section an examination of the curious particulars in which his results for the steam-engine, or the air-engine, differ from those now received.

26. If we carefully examine the above cycle of operations we easily see that they are *reversible*, i.e. that the transference of the given amount of caloric back again from *B* to *A*, by performing the same operations in the opposite order, requires that we expend on the piston, on the whole, as much work as was gained during the direct operations. This most important idea is due to Carnot, and from it he deduces his test of a *perfect* engine, or one which yields from the transference of a given quantity of caloric from one body to another (each being at a given temperature) the greatest possible amount of work. And the test is simply that *the cycle of operations must be reversible*.

To prove it we need only consider that, if a heat-engine *M* could be made to give more work by transferring a given amount of caloric from *A* to *B*, than a reversible engine *N* does, we may set *M* and *N* to work in combination, *M* driven by the transfer of heat, and in turn driving *N*, which is employed to restore the heat to the source. The compound system would thus in each cycle produce an amount of work equal to the excess of that done by *M* over that expended on *N*, without on the whole any transference of heat, which is entirely contradictory of experience.

Carnot, therefore, proved, upon his assumptions, that the ratio of the work done by a perfect (*i.e.* a reversible) engine to the heat taken from the source is a function of the temperatures of the source and condenser only; because no mention is necessarily made of any particular substance. When these temperatures are nearly equal, this function is expressible by the product of their difference into a function of either, which is called *Carnot's Function*.

W. Thomson, so early as 1848,<sup>1</sup> seized upon this remarkable proposition, and made it the basis of the earliest suggestion of an *absolute* Thermometric Scale; absolute in the sense of being based upon strict thermodynamic principles, and entirely independent of the properties of any particular substance. This extremely valuable suggestion will be carefully considered in our third chapter.

27. The remarkable consequences deduced by W. Thomson, by a combination of the methods and results of Fourier and Carnot, with reference to the *Dissipation* of heat, and the final transformations of all forms of energy, though properly belonging to this part of the development of the subject, are left to a future page, so that the chronological order may be adhered to as closely as possible in presenting the most important additions to the science.

28. A little before the publication of Carnot's work, a second method of procuring mechanical effect from heat was discovered by Seebeck. It consists in the production of electro-motive force by the action of heat on heterogeneous conducting matter, and the employment of the current thus produced to move a galvanometer needle; or, in later improvements, to drive an electro-magnetic engine. It is not alluded to by Carnot; and it will tend greatly to the simplicity of this explanatory narrative if the consideration of the other physical agents, which the grand principle of conservation of energy has shown to be so intimately

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<sup>1</sup> *Proc. Camb. Phil. Soc. (Phil. Mag. 1848).*

related to heat, be deferred to another chapter. We shall, therefore, at present, confine ourselves as strictly as possible to the relation between heat and mechanical effect, which is, however, only one branch of the dynamical theory.

29. Clapeyron, in 1834,<sup>1</sup> recalled attention to Carnot's reasoning, and usefully applied the principle of Watt's diagram of energy to the geometrical exhibition of the different quantities involved in the cycle of operations by which work is derived from heat by the temporary changes it produces in the volume or molecular state of bodies. He also, first, gave a representation of Carnot's processes in an analytical form. But for nearly twenty years after the appearance of Carnot's treatise little appears to have been done with reference to the *theory* of heat.

30. Then there appeared, almost simultaneously, a group of three or four speculators and experimenters whose relative claims have been since pressed, in some cases, with considerable warmth, though it seems not very difficult to estimate them so far as the discovery either of the true theory, or the mechanical equivalent, of heat is concerned. In 1837, Mohr<sup>2</sup> pointed out very clearly many of the necessary consequences of the establishment of the undulatory nature of radiant heat ; and showed how the work-equivalent of heat might be found from the two specific heats of air. In 1839, Séguin, a relative of the celebrated Montgolfier (from whom indeed he says he derived his ideas on the subject of heat), in a very curious work on railways,<sup>3</sup> gave data from which it is easy to deduce 650 kilogrammètres<sup>4</sup> as the mechanical equivalent of heat.<sup>5</sup> In 1842, Mayer<sup>6</sup>

<sup>1</sup> *Journal de l'Ecole Royale Polytechnique*, vol. xiv. (*Scientific Memoirs*, I.)

<sup>2</sup> Liebig's *Annalen—Ansichten über die Natur der Wärme*. Translated in *Phil. Mag.* August 1876.

<sup>3</sup> *Sur l'Influence des Chemins de Fer*.

<sup>4</sup> That is, a kilogramme of water must fall 650 mètres to have its temperature raised by 1° C.

<sup>5</sup> *Phil. Mag.* Oct. 1864.

<sup>6</sup> Liebig's *Annalen*.

assigned 365 kilogrammètres for the value of that physical constant. It is curious to observe that the methods employed by the two latter were almost identical: that of Séguin being founded on the principle that the work given out by any body dilating, and thereby losing heat, is the equivalent of the heat lost; while that of Mayer is, that the heat developed by compression is the equivalent of the work expended in compressing the body. Neither makes the slightest limitation as to the nature of the substance to be experimented on, both their statements are perfectly general; and, it may be added, not only inaccurate, but (with certain exceptions) not even roughly approximate.<sup>1</sup> Mayer professes to found his process on a species of metaphysical reasoning as to the indestructibility of force (*Kraft*); we have already seen what value is to be attached to speculations of this nature.<sup>2</sup> Besides, Mayer gives, as an analogy to the compression of a body and the consequent production of heat, the fall of a stone to the earth or the impact of a number of gravitating masses, and the consequent heating of all. This, it need scarcely be said, is inadmissible. His hypothesis *might* possibly have been a law of nature, but it never could have had any analogy with the gravitation case

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<sup>1</sup> Séguin and Mayer have still followers. For instance—‘Qu’un gaz ou tout autre corps soit réduit, par le travail dû à des forces extérieures, à diminuer de volume, il y aura en même temps production d’une quantité de chaleur qui sera dans le même rapport constant avec le travail mécanique dépensé.’—Combes, *Théorie Mécanique de la Chaleur*. Paris, 1867, 8vo.

<sup>2</sup> Mayer does not accept the conclusions deduced by Davy and Rumford from their experiments, and now almost universally received. He says, ‘Wir möchten vielmehr das Gegentheil folgern, dass um zu Wärme werden zu können, die Bewegung—sey sie eine einfache, oder eine vibrirende, wie das Licht, die strahlende Wärme, etc.,—*aufhören müsse, Bewegung zu seyn.*’ Thus, according to Mayer, heat is *potential energy*, unless indeed there be some mysterious *tertium quid*. For a farther examination of this question, and especially for the opinions of Joule and Colding upon the so-called claims of Mayer, see Tait, *Recent Advances in Physical Science*.

he compares it to. Besides, so far as air is concerned, the hypothesis had been given only *five* years before by Mohr in the very same journal. Mayer does not even allude to Mohr's paper.

31. But what it most concerns us to note here is, that all three entirely ignore Carnot's fundamental principle, viz., that no deduction whatever can be made as to the relation between heat and mechanical effect, when the body operating or operated upon is in different states at the beginning and end of the experiment.<sup>1</sup> Take, for instance, the second operation in the cycle of Carnot as above explained. Yet it is to be observed that Séguin distinctly pointed out that steam, which has done work in an engine, ought not to heat the water in the condenser so much as if it had been directly led into it; and made numerous but indecisive experiments to prove the truth of this statement (conclusively verified by Hirn in 1862).

32. The numerical data requisite for the application of either of these erroneous methods were known at the time for only one or two bodies, and, even for these, very inaccurately. So that it is not at all remarkable that the equivalents above given are far from exact. Séguin reasoned from steam, Mohr, and after him Mayer, from air. It happens that this paucity of data led Mayer to choose a substance which Joule afterwards experimentally proved to be capable of giving, even with the erroneous hypothesis, a result not far from the truth; but, even if Mayer had in 1842 possessed accurate data, and had therefore been fortunate enough to obtain an approximate result instead of a very inexact one, his determination could never have been correctly called more than a happy guess founded upon a total neglect of sound reasoning. It has been stated by some writers that Mayer is the author of the Dynamical Theory of Heat; and that he deduced in 1842, by a simple

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<sup>1</sup> Thomson, *Trans. R.S.E.* 1851, p. 291, Note.



calculation, as accurate a value of the dynamical equivalent as Joule arrived at in 1849, after seven years of laborious experiment. It is difficult to perceive the grounds on which such statements are made. The dynamical theory, as we have already seen, was established by Davy and Rumford. Mayer, three years later than Séguin, and five years later than Mohr, enuntiated and applied, like them, a false principle, and got (from the experiments of others on the specific heats of air) a widely erroneous result, which was improved, not by its author but by Joule, two or three years afterwards; who, after finding the true result by a legitimate process, *proved* by experiments on air<sup>1</sup> that Mayer ought to have got a good approximation.

33. Another of the group is Colding, a Danish engineer, whose results were published in 1843.<sup>2</sup> He appears to have been led by a species of metaphysical reasoning to the idea of the conservation of energy; but, unlike some other speculators, to have appealed to experiment before publishing his views. The value (350 kilogrammètres) of the equivalent of heat which he thus obtained from friction experiments, is not much more accurate than that deduced from Rumford's data,—and is not to be compared with Joule's of the same year. Still Colding evidently went to work in the right way, and deserves an amount of credit to which Mohr, Séguin, and Mayer have no claim.

34. It must be premised that much of Joule's work (which dates back as far as 1840 in the *Proc. R.S.*) has reference to the general theory of conservation of energy, and that his first determinations of the dynamical equivalent of heat were obtained by means of the magneto-electric machine, so that, in accordance with the definite object of the present chapter, only such of his investigations will be now noticed as strictly bear on the *immediate* relation between heat and mechanical effect.

<sup>1</sup> *Phil. Mag.* 1844, ii.

<sup>2</sup> *Phil. Mag.* Jan. 1864.

35. His earliest published experiments of this class are described in the appendix to a paper published in 1843 in the *Philosophical Magazine*, having been read before the British Association at its meeting in Cork. The valuable discoveries contained in this paper do not properly belong to the present subject, but will be carefully considered in the second chapter. In the appendix, however, there is described an experimental method of *directly* determining the mechanical equivalent of heat, so simple, and yet so effective, as to deserve careful consideration. It consisted in working up and down in a closed cylinder, filled with water, a piston formed of a number of capillary tubes bound together, so as to constitute a mass with visible pores. The friction of the water when forced to pass through these tubes of course developed heat, which, as well as the work spent in moving the piston, was carefully measured. It is very remarkable that, from the series of experiments, agreeing well with one another, which were made with this simple apparatus, Joule deduced as the dynamical equivalent of heat (that is, of the heat required to raise the temperature of a pound of water 1° F.)

770 foot-pounds,<sup>1</sup>

differing by only about a quarter per cent. from the results of his subsequent and far more elaborate determinations. The close agreement of the results of successive trials was quite sufficient to justify him in publishing this, as in all probability a very close approximation to the desired value of the equivalent.

[It is curious that the mean of the values deduced from

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<sup>1</sup> To compare this with the estimates of Séguin and Mayer, and the result of Colding, we must remember that a mètre is 3·28 feet, and a centigrade degree  $\frac{9}{5}$ ths of a degree Fahrenheit, while the unit of heat is capable of raising the temperature of a kilogramme of water by 1° C. So that Joule's numerical result, expressed in kilogrammètres, is  $\frac{9 \times 770}{5 \times 3 \cdot 28} = 422$  nearly.

Rumford's and Colding's experiments, the two legitimate ones whose publication preceded that of this result of Joule's, differs from it by only about  $2\frac{1}{2}$  per cent.]

36. Before leaving this part of our subject it may be desirable to complete the enumeration of the results of Joule's direct experiments for the determination of the mechanical equivalent, as they are certainly superior in accuracy to those of any other experimenter.

Repeating in 1845 and 1847 his experiments on the friction of water—but now by means of a horizontal paddle, turned by the descent of known weights—he obtained results gradually converging, as in each successive set of experiments extraneous causes of error were more completely avoided or allowed for. The value of the equivalent deduced in 1847 from a great number of experiments with water was 781·5 foot-pounds, and with sperm oil, 782·1. In the paper of 1845, we find his first speculations as to the absolute zero of temperature, or the temperature of a body absolutely deprived of heat. The most interesting of his results are, that the absolute zero of temperature is  $480^{\circ}$  Fahr. below the freezing-point of water, and that a pound of water at  $60^{\circ}$  Fahr. possesses, in virtue of its heat, mechanical energy to the enormous amount of at least 415,000 foot-pounds. Changes have since been shown to be necessary in these numbers, but they are comparatively unimportant. And it must be regarded as one of the most extraordinary results of physical science, that a pound of water at ordinary temperatures contains heat capable (if it could be applied) of raising it against gravity to a height of at least 80 miles.

37. Finally, in 1849, Joule published the results of his latest and most elaborate experiments, of which, after what has been already said, the results only need be given:—

From friction of Water,	772·692 foot-pounds.	
„ „ Mercury,	774·083	„
„ „ Cast-iron,	774·987	„

The conclusions of this valuable paper, after all allowance is made for slight but inevitable losses of energy, by sound and other vibrations, are thus given :—

1st, *The quantity of heat produced by the friction of bodies, whether solid or liquid, is always proportional to the quantity of work expended.*

2d, *The quantity of heat capable of increasing the temperature of a pound of water (weighed in vacuo, and taken at between 55° and 60°) by 1° Fahr., requires for its evolution the expenditure of a mechanical force represented by the fall of 772 lbs. through the space of one foot.*

It is only necessary to observe, that the determination is for the value of gravity at Manchester, and must of course be diminished for higher, and increased for lower latitudes, according to the well-known law.

38. As no one has yet pretended to rival in accuracy the experiments of Joule above mentioned, and as his celebrated result of 1843, so very close to the truth, preceded all other recent sound attempts to determine the mechanical equivalent of heat, the results of *direct* methods since employed by other observers may be passed over, with the remark, that they agree more or less perfectly with those of Joule.

39. We now come to the consideration of the method suggested by Mohr, Séguin, and Mayer, with which Joule seems to have occupied himself experimentally in 1844. We shall briefly describe his experiments, though not in the order in which they were made, this change being required for the continuity of our exposition. Joule, repeating in a greatly improved form an old experiment of Gay Lussac, compressed air to twenty atmospheres or so in a strong vessel, which was afterwards screwed to another previously exhausted. A very perfect stop-cock prevented all passage of air from one to the other until it was desired. The whole was placed in a vessel of water, which was stirred to bring it to a uniform temperature. On opening the stop-

cock, the air rushed from the first vessel to the second, so that in a short time the pressure was the same in both. On measuring the temperature of the surrounding water again, *no change was perceptible*,<sup>1</sup> at least after the proper corrections, determined by separate experiments, had been made for the amount of heat produced by the stirring, etc., during the operation. This is a *most important* result, as will be shown immediately, though it is as well to say at once that it is not absolutely exact, as is proved by subsequent experiments capable of even greater accuracy than that just described. The condensed air has been allowed to expand without doing work on external bodies, and though its volume has been greatly increased, no heat has been lost, though we might have imagined such would be the case. From this we are entitled to conclude, that the heat developed by compressing a gas is (to the amount of approximation already mentioned) the equivalent of the mechanical effect expended in the compression, and thus that the assumption made by Mohr, Séguin, and Mayer, unwarrantable as it is for bodies in general, is very nearly true for air. Why, then, was Mayer's value of the mechanical equivalent so erroneous? Simply because the direct determination of the specific heat of air is an exceedingly difficult and delicate operation, and had been only very roughly effected before 1842. Rankine and Thomson first theoretically assigned the true value, founding their calculations on Joule's experimental results from the friction of fluids. ¶Joule, by a direct experiment, obtained a closely accordant value; and finally Regnault, also by direct experiment, obtained *exactly* the number predicted from theory.

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<sup>1</sup> In Gay Lussac's experiment, the temperatures were measured by thermometers suspended in the centre of each vessel. One was observed to rise as much as the other fell; but it was found that very different effects were produced when the thermometers were not in the centres of the vessels; so that no *quantitative* deduction could be made from the experiment.

40. What actually took place in Joule's experiment was, the air in the first vessel, suddenly expanding, produced mechanical effect in forcing a portion of its mass with great velocity into the second vessel; this it did at the expense of its store of energy in the form of heat. Thus the first vessel was *cooled* to a certain extent. The air rushing into the second vessel produced, by friction against the connecting tube and the sides of the vessel, and amongst its own particles, and by the condensation produced by each successive arrival of air upon all which preceded it, a development of heat. Thus the second vessel was *heated*. Now it is obvious that we are not at liberty (without experimental proof) to assume that the loss of heat in the first vessel will be exactly, or even nearly, equal to the gain in the second. But as experiment has shown them to be almost equal, either the heat produced by condensing air, or the cold produced by its expansion from a condensed state, may legitimately be taken as one of the data for an approximate determination of the mechanical equivalent. The last cited paper of Joule's contains five sets of careful experiments made for this purpose by one or other of these methods. The extreme results are 823 and 760 foot-pounds respectively; the mean of the last three sets, chosen as the most likely to be correct, giving the number 798 foot-pounds—only about  $3\frac{1}{2}$  per cent. too great.

The student ought carefully to notice here that the process employed in Joule's experiment (§ 39) is essentially an irreversible one. The expanded gas has lost no heat to external bodies, and it has done no external work, yet its power of doing work has been notably diminished, and it could not be restored to its original condition without expenditure of work from an independent source, and subsequent removal of an equivalent amount of heat. In fact, the whole energy contained in the gas remains unchanged in amount, but part of its *convertibility into work* has been

lost. This will be more easily understood when we have considered the Dissipation of Energy.

41. It may now be asked, does the dynamical theory of heat necessitate any serious change in the important results deduced by Carnot from the caloric hypothesis? This question was answered with greater or less detail in 1849, 1850, and 1851 respectively, by Rankine, Clausius, and W. Thomson.

42. Rankine's first investigation of the principles of the mechanical action of heat appeared in a paper received by the Royal Society of Edinburgh in December 1849, and read in February 1850.<sup>1</sup> It is based on what he calls the 'Hypothesis of Molecular Vortices;' that is to say, the supposition that the motions of which Davy showed thermometric heat to consist are of the nature of vortices, whirls, or circulating streams. That is the part of the hypothesis which is specially connected with the phenomena of the mechanical action of heat; but in order to connect these with some other phenomena, Rankine makes the further supposition, that the whirling matter is diffused in the form of atmospheres round nuclei, which may be either bodies of a special kind, or centres of condensation and attraction in the atmospheres; and that radiance, whether of heat or light, consists in the transmission of a vibratory motion of the nuclei, by means of forces which they exert on each other. The quantity of heat in a body is the energy of its molecular vortices; the absolute temperature of the body is the same energy divided by a specific co-efficient for each particular substance. A perfect gas is a substance in which the elastic pressure is sensibly that which varies with the centrifugal force of the vortices only; and the intensity of that pressure, according to the known principles of mechanics, must be proportional directly to the energy of the vortices and inversely to the space that they

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<sup>1</sup> *Transactions*, vol. xx. p. 147.

occupy. In substances not perfectly gaseous the elasticity is modified by attractive or cohesive forces. When the deviation from the perfectly gaseous state is small, the effects of such forces may be approximately represented by series in terms of the reciprocal of the absolute temperature.<sup>1</sup>

43. Sensible heat, according to Rankine, is the energy employed in varying the velocity of the whirling particles; latent heat, the work done in varying the dimensions of their orbits when the volumes and figures of the spaces in which they whirl are changed. The force which keeps any particle in its orbit is equal and opposite to the centrifugal force of that particle; therefore the work done in varying the orbits of the particles is proportional to their centrifugal force; therefore to the energy of the vortices; therefore to the absolute temperature; and to compute that quantity of work, or latent heat, when a body undergoes a given variation of dimensions, the absolute temperature is to be multiplied by the corresponding variation of a certain function of the dimensions and elasticity of the body; which function is computed by taking the rate of variation with temperature, of the external work done during the kind of change of dimensions under consideration. Such is an outline of the method by which Rankine deduces the *general equation of the mechanical action of heat*, from the Hypothesis of Molecular Vortices, by means of known dynamical principles.

44. The quantity whose variation, being multiplied by the absolute temperature, gives the latent heat corresponding to a given change of dimensions at that temperature, is expressed in Rankine's earlier papers by symbols, but is not designated by a special name. In a paper, read in January 1853,<sup>2</sup>

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<sup>1</sup> Rankine had previously published an example of the use of such series in a paper on the 'Elasticity of Vapours,' *Edin. Phil. Journal*, July 1849, and he also applied them with success to the elasticity of carbonic acid, and some other gases.—*Phil. Mag.* Dec. 1851.

<sup>2</sup> *Trans. R.S.E.* vol. xx. p. 569.



he proposes the name 'Heat-Potential;' and in a paper received by the Royal Society of London in December 1853, and read in January<sup>1</sup> 1854, he gives to the same quantity, with a certain additional term depending on change of temperature, the name of 'Thermodynamic Function;' a name which has since been adopted by various other authors. In Rankine's paper of 1849, the chief applications of the general equation of thermodynamics are as follows:—The values of apparent as distinguished from real specific heat, for gases and vapours under various circumstances; the demonstration that the apparent specific heat of a vapour kept constantly at the pressure of saturation while its volume varies is negative for most fluids at ordinary temperatures; in other words, that steam (for example) tends to become partially liquefied when it works expansively, contrary to what had been previously believed; and the demonstration that the total heat of evaporation of a perfect gas increases with temperature at a rate equal to the specific heat of the gas at constant pressure. In a paper read on the 2d December 1850,<sup>2</sup> he deduced from Joule's Equivalent the value 0.24 for the specific heat of air at constant pressure, and concluded that the previously received value, 0.2669 must be erroneous; this was verified by Joule's experiments, communicated to the Royal Society on the 23d of March 1852, and by Regnault's experiments, communicated to the Academy of Sciences in 1853. In a paper read on the 21st April 1851,<sup>3</sup> he deduced from the general equation of thermodynamics, as given in his paper of 1849, Thomson's law (§ 54 below) of the efficiency of a perfect heat engine:—that the whole heat expended is to the heat which disappears in doing mechanical work, as the absolute temperature at which heat is received to the difference between the temperatures at which heat is received and rejected.

45. In Rankine's paper of 1849, groups of circular

<sup>1</sup> *Phil. Trans.* 1854.

<sup>2</sup> *Trans. R.S.E.* vol. xx. p. 191.

<sup>3</sup> *Ibid.* p. 205.

vortices were supposed to be arranged in spherical layers round the atomic nuclei, in order to simplify the investigation. On the 18th December 1851 he read a paper,<sup>1</sup> in which it is shown that precisely the same results as to the relation between heat, elasticity, and mechanical work follow from the supposition of molecular vortices of any figure arranged in any way.

In a long series of papers he applied the principles of thermodynamics to various practical questions relating to the steam-engine and other heat engines; and he was the author of the first separate treatise in which the science of thermodynamics was set forth with a view to its practical application.<sup>2</sup>

We have treated Rankine's theoretical investigations at considerable length here, because they are founded on a peculiar hypothetical basis; and, so far as *method* is concerned, are widely separated from those of Clausius, Thomson, and others, which have among them some slight resemblance as regards fundamental assumptions and mode of investigation.

46. The first paper of Clausius<sup>3</sup> on the Mechanical Action of Heat was read to the Berlin Academy of Sciences in February 1850, and printed in Poggendorff's *Annalen* for March and April of the same year. It is divided into two parts; the first relating to the mechanical action of heat in perfect gases; the second to the mechanical action of heat in substances in general. In the *first part*, Clausius makes use of the first law of thermodynamics only, viz., that of the equivalence of heat and mechanical work, without any reference to a second law; and thus he arrives at a general equation of the mechanical action of heat in perfect gases,

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<sup>1</sup> *Trans. R.S.E.*, p. 425.

<sup>2</sup> *A Manual of the Steam-Engine and other Prime Movers*, 1859.

<sup>3</sup> His papers are collected as *Abhandlungen über die mechanische Wärme-theorie*. Leipsic, 1864-7 (2d ed., 1876). See also *Clausius on Heat*, Van Voorst, 1867.

containing a certain unknown function. He endeavours to distinguish between the external work done by an elastic substance in expanding against external pressure, and what he calls the *internal work* done by the particles of the body in altering their relative positions against the cohesive forces which they exert on each other; and he states, as being highly probable, Mayer's hypothesis, modified as follows; *in perfect gases the internal work is inappreciably small.* This supposition enables him to assign a definite form to the function which was unknown in the previous equation, and so to obtain a more definite equation for the mechanical action of heat in perfect gases; and from the latter equation he deduces various results which are in conformity with experiment.

47. In the *second part* of the paper, Clausius for the first time makes use of 'Carnot's Law,' modified in such a way as to bring it into harmony with the fact of the equivalence of heat and mechanical energy; viz., that when a substance performs mechanical work, by going through a reversible cycle of changes at the end of which it returns to its original condition, the ratio borne by the quantity of heat which disappears in performing work, to the whole quantity of heat expended, is a function solely of the temperatures at which the changes take place. By combining Carnot's law, as thus modified, with the results obtained in the first part of the paper, involving the supposition that the internal work in perfect gases is inappreciable, he arrives at the conclusion that the probable value of 'Carnot's Function'<sup>1</sup> is the reciprocal of the absolute temperature as measured on a perfect gas thermometer; and thus he obtains the mathematical expression of the second law of thermodynamics, as the expression of three principles combined, viz. :—

(1.) The equivalence of heat and mechanical work ;

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<sup>1</sup> The same law had been previously suggested by Joule as probable in a private letter to Thomson, dated 9th December 1848. (See also § 54 below.)

(2.) The principle of Carnot, modified to harmonise with that of the equivalence of heat and mechanical work ;

(3.) Séguin and Mayer's hypothesis restricted to permanent gases (and since proved to be very approximately true for them by the experiments of Joule and Thomson).

48. Clausius applies his general equations to the evaporation of liquids ; and arrives, amongst other results, at the conclusion that most saturated vapours, when working expansively at ordinary temperatures, tend to become partially liquefied ; a conclusion arrived at simultaneously (§ 44) by Rankine.

49. Passing over some papers relating to matters of detail connected with the mechanical theory of heat, the next paper of Clausius in which fundamental principles of that theory are investigated, is 'On an altered form of the second law of the mechanical theory of heat.'<sup>1</sup> The peculiar form of the second law of Thermodynamics here referred to (but which was first given by Thomson in 1851,—see Chap. III.) is called by the author 'the Law of the equivalence of transformations.' It is expressed in words to the following effect—that 'In all cases in which a quantity of heat is transformed into work, and the bodies by means of which that transformation is effected return at the end of the operation to their original condition, another quantity of heat must at the same time pass from a hotter to a colder body ; and the proportion which the latter quantity of heat bears to the former depends solely upon the temperatures of the bodies between which it passes, and not upon the nature of the intervening bodies.' This is evidently Carnot's principle, adapted to the mechanical theory of heat, and expressed in a different way. In this paper Clausius investigates the properties of a function which he calls *Aequivalenzwerth*, and whose value is found by dividing the quantity of heat expended in producing a given change in a given substance by a certain function of the temperature at which that change

<sup>1</sup> *Pogg. Ann.* Dec. 1854. *Abhandlungen*, p. 127.

takes place ; which function of temperature Clausius shows, from the probability that internal work in perfect gases is inappreciable, to be probably proportional simply to the absolute temperature, as measured by a perfect gas thermometer. (The Aequivalenzwerth of Clausius is nearly identical with the Thermodynamic function of Rankine ; but there are some points of difference which are explained in the later papers of Clausius.)<sup>1</sup> The properties of the function here called Aequivalenzwerth, and in later papers *Entropie* (closely connected with Thomson's previously published Theory of Dissipation), form the subject of a long series of investigations. The special investigations of Clausius as to the internal work, and his function called the *Disgregation*, will be briefly considered in the third chapter.

50. 'The investigations of both these writers fundamentally involve various hypotheses, which may or may not be found by experiment to be approximately true, and which render it difficult to gather from their writings what parts of their conclusions, especially with reference to air and gases, depend merely on the necessary principles of the dynamical theory.'<sup>2</sup>

51. One of the most valuable of the results which, as we have just seen, was obtained almost simultaneously by Rankine and Clausius, is as follows :—If saturated steam at any high temperature is allowed to expand, pressing out a piston, in a vessel impervious to heat, it cools so as to keep always at the temperature of saturation ; and, besides, a portion of it liquefies. This result appears at first sight inconsistent with the paradoxical experiment long known, that high-pressure steam escaping into the air through a small orifice does not scald the hand, or even the face, of a person exposed to it ; while, on the contrary, low-pressure steam inflicts fearful burns. W. Thomson has explained

<sup>1</sup> See Rankine 'On Thermodynamic and Metamorphic Functions, Disgregation, and real Specific Heat.'—*Phil. Mag.* Dec. 1865.

<sup>2</sup> Thomson, *Trans. R.S.E.* 1851, p. 281.

the difficulty thus : The steam rushing through the orifice produces mechanical effect, immediately wasted in fluid friction, and consequently *reconverted into heat*, from which, by Regnault's numerical data, it follows that the issuing steam (in the case of the high-pressure, but not of the low-pressure, boiler) must be over  $212^{\circ}$  Fahr. in temperature, and *dry*.

52. In its new form, the theory of the motive power of heat is based upon the two following propositions : the first of which, though really announced by Davy, was only definitely received in science in consequence of Joule's experiments ; the second is the proposition of Carnot (already given, § 26, with its demonstration on the caloric theory), adapted by Thomson to the dynamical theory.

I. When equal quantities of mechanical effect are produced by any means whatever from purely thermal sources, or lost in purely thermal effects, equal quantities of heat are put out of existence, or are generated.

II. If an engine be such that, when it is worked backwards, the physical and mechanical agencies in every part of its motions are all reversed, it produces as much mechanical effect as can be produced by any thermodynamic engine, with the same temperatures of source and refrigerator, from a given quantity of heat.

53. In order to prove the second proposition (which regards the *Transformation* of heat, as the first regards the *Conservation* of energy), we must consider in what respect Carnot's proof has become inapplicable, and we find it to be this : we have no right *now* to assume, as he did, that in a complete cycle of operations in which his fundamental condition is satisfied (*i.e.* the medium brought exactly to its primitive state) as much heat has been given out to the refrigerator as has been absorbed from the source ; because the first of our new propositions shows that this is only true when the medium has had as much work done upon it as it has exerted on external bodies. Clausius attempted to prove the proposition in 1850, by a process strictly analo-

gous to that of Carnot already given, but based solely on the observed fact that heat tends to pass from warmer to colder bodies. Some years later<sup>1</sup> he asserts that in this passage he had assumed the following axiom, '*It is impossible for a self-acting machine, unaided by any external agency, to convey heat from one body to another at a higher temperature.*' Thomson<sup>2</sup> in 1851 gave a satisfactory proof based on the axiom, that '*It is impossible, by means of inanimate material agency, to derive mechanical effect from any portion of matter by cooling it below the temperature of the coldest of the surrounding objects.*'

In fact, we see by § 26 that, if we make  $N$  transfer back to the source a quantity of heat equal to that taken from it by  $M$ , the compound system could only do work by  $N$ 's taking more heat from the refrigerator than  $M$  gives to it.

Thomson introduces his assumption in an exceedingly guarded way, and this course has since been fully justified by Clerk-Maxwell, who has shown that, if the molecules of hot bodies are in a state of motion with unequal velocities, finite beings, without any expenditure of work, could under conceivable conditions transfer heat from a cold body to a hot one; and that the process actually goes on, though to a very small extent, in every mass of gas.<sup>3</sup>

54. Carnot showed that, on his principles, the amount of work done by the transference of a given amount of heat increases indefinitely with the increasing difference of temperatures of the source and refrigerator; and of course it follows from this that the air-engine, in which a much greater range of temperature may be employed with safety than in the steam-engine, should be the more effective of the two. The introduction of the true theory leaves this

<sup>1</sup> *Abhandlungen*, p. 50; with date 1864. See *Phil. Mag.* 1872, i. pp. 106, 338, 443, 516; and ii. 117, 240.

<sup>2</sup> *On the Dynamical Theory of Heat*, etc., by W. Thomson, *Trans. R.S.E.* March 17 and April 4, 1851.

<sup>3</sup> See Tait, *Recent Advances in Physical Science*.

result unaffected except in *degree* ; in fact it shows that the work to be derived from a given amount of heat leaving the source increases indeed with the excess of temperature of the source over the reservoir ; but, far from increasing indefinitely as Carnot's theory showed, it has as a superior limit, which it never reaches, the mechanical equivalent of the heat which leaves the source. In fact, temperature is now defined by the statement that in the working of a reversible heat-engine the ratio of the heat taken in to that ejected is that of the *absolute* temperature (§ 36) of the source to the *absolute* temperature of the refrigerator.<sup>1</sup> We may consider either the proposition that a reversible engine is perfect, or the definition of temperature which that proposition has enabled us to give, as the Second Law of Thermodynamics. A great many attempts have of late been made to show that this second law is merely a form of Hamilton's Principle of *Varying Action*—a pure principle of dynamics. It is obvious, from the fact that if we could at any moment exactly reverse the motion of every particle, we should make a dynamical system (however complex) go back through all its previous states of motion, that such a deduction from Hamilton's principle can only be made by a method of averages which virtually *assumes* the degradation of energy, a consequence of the law to be proved.

Thus, in the most favourable circumstances, the steam-engine, and even the air-engine, are exceedingly imperfect ; giving at most only about one-fourth of the mechanical equivalent of the heat spent. The theory of what have been called Caloric Engines, where ether, or chloroform, or some such easily vaporised liquid, is used in connection with air or steam to utilise as much as possible of the applied heat, has been given by various investigators, including those last mentioned, but it appears that in practice the method has not realised the anticipations of its proposers.

55. A most remarkable result of the application of

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<sup>1</sup> W. Thomson, *Trans. R.S.E.* 1851.



Carnot's reasoning was given by J. Thomson in 1849.<sup>1</sup> From this reasoning it is obviously demonstrable, as shown by W. Thomson, that *water at the freezing-point may, without any expenditure of work on the whole, be converted into ice by a mechanical process.* For a mass of water retains the temperature of freezing unchanged until it is all converted into ice, and according to Carnot's, and even to the dynamical, theory, no work is required to make heat pass from one body to another at the same temperature. J. Thomson first remarking that this result seemed to involve the possibility of producing work from nothing (since water *expands* with great power in the act of freezing), was led, on the only way of escape from a conclusion which no naturalist could admit, to the conclusion that the temperature at which water freezes must depend, as the boiling-point had long been known to do, upon the pressure; and he showed that the freezing-point of water must be *lower* by  $0^{\circ}\cdot 0135$  Fahr. for each additional atmosphere of pressure. This very curious theoretical deduction was verified, to its numerical details, by means of Ørsted's Piezometer, by W. Thomson,<sup>2</sup> and it has been successfully applied by the Thomsons and Helmholtz to explain the extraordinary plasticity of glacier ice discovered by the careful measurements of Forbes. Hopkins and Bunsen have since verified experimentally another consequence of the same theory, viz., that in cases where bodies *contract* on solidifying, as is the case with sulphur, wax, etc., the melting-point is *raised* by increase of pressure.

56. The complete theory of all such cases had, however, been previously given by W. Thomson, who was the first (after Clapeyron) to recall attention to the work of Carnot; developing many of its more important consequences so far that the form, for instance, of Carnot's function follows at once from his paper, if the conversion of heat into work be

<sup>1</sup> *Trans. R.S.E.* 1849.

<sup>2</sup> *Proc. R.S.E.* 1850.

assumed. He seems to have been at first unwilling to encounter the new problems suggested by the true theory,<sup>1</sup> but having in 1851 obtained a satisfactory basis for the Second Law, he advanced with tremendous strides, leaving (so far as the theory has yet been developed) little but practical applications or experimental verifications of his results to be made by his contemporaries. Dissipation, Restoration, General Laws of Transformation, Thermo-electricity, Magnecrystallic action, etc. etc., were all comprehensively investigated by him in little more than a year. It is greatly to be regretted that Thomson's scattered papers, which, while models of brevity and distinctness, evince a marvellous clearness of perception, and, above all, are always based directly upon ascertained facts,<sup>2</sup> have not been reprinted in a collected form. Till this is done, few will be aware, either of the immense extent to which he has pushed the theory, or of the number of discoveries in which he anticipated those to whom they are usually assigned. In so elementary a work as the present, many of the most important of these points must be passed over with the merest allusion.

57. In his (already cited) paper of 1851, on the Dynamical Theory of Heat, without encumbering himself with,

<sup>1</sup> 'If we [abandon Carnot's fundamental axiom, a view which is strongly urged by Mr. Joule] we meet with innumerable other difficulties, insuperable without farther experimental investigation, and an entire reconstruction of the theory of heat, from its foundation.'—(*Trans. R.S.E.*, 1849, p. 545, Note.)

<sup>2</sup> 'Unter den Naturforschern, welche ihr Streben vorzugsweise darauf gerichtet haben, die Naturwissenschaft von allen metaphysischen Erschleichungen und von allen willkürlichen Hypothesen zu reinigen, sie im Gegentheil immer mehr zum reinen und treuen Ausdruck der Gesetze der Thatsachen zu machen, nimmt Sir W. Thomson eine der ersten Stellen ein, und er hat gerade dieses Ziel vom Anfange seiner wissenschaftlichen Laufbahn an in bewusster Weise verfolgt.'—Helmholtz, Preface to the German edition of Thomson and Tait's *Natural Philosophy*.

or limiting the generality of his results by, any hypothesis, Thomson applies the fundamental propositions of the dynamical theory (already given) to all bodies, and deduces many very curious and important results regarding the specific heats of all substances; with special conclusions agreeing with those of Rankine and Clausius for 'perfect' gases, and for mixtures of portions of a body in different states but at the same temperature, as ice and water, or water and saturated steam. Among these we may mention the following:—When a substance contracts as its temperature rises (as is the case, for instance, with water between its freezing-point and its point of maximum density), its temperature will be *lowered* by a sudden *compression*. In two most valuable experimental papers<sup>1</sup> by Joule, Thomson's formulæ are completely verified (within the limits of experimental error) for substances of the most dissimilar qualities. One very curious result is afforded by india-rubber, which, when suddenly extended, becomes warm; and, in agreement with Thomson's conclusions, is found, when stretched by a constant weight, to contract on being heated, and to raise the weight.

58. We have several times alluded to the fact, that the amount of heat developed by the compression of air is only *approximately* equal to the equivalent of the work expended in compressing it, although in Joule's experiment of 1844 it appeared to be *exactly* equal to it. There is, as before observed, no *à priori* reason for the existence of any such equality, unless we assume the kinetic theory of gases to be true, and that there are no internal forces (though Clausius considers it to be a probable deduction, in the case of a non-liquefiable gas, from the laws of Boyle and Charles as to the relations between pressure, volume, and temperature), for it is quite conceivable that a gas or

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<sup>1</sup> *On some Thermo-dynamic Properties of Solids, and On the Thermal Effects of compressing Fluids.*—*Phil. Trans.* 1859.

other body might exist in which the whole work expended in compressing it, is employed in overcoming repulsive forces among its particles, and would therefore be wholly stored up as mechanical power in the compressed gas, without any change of temperature whatever. That heat, nearly equivalent to the work expended in compression, is actually developed, shows us that the mutual molecular forces among particles of a gas are exceedingly small, and that the pressure of a gas is due almost entirely to the 'repulsive motion' of Davy.

59. Daniel Bernoulli, in the tenth section of his *Hydrodynamica*, explains the pressure of air by the impact of its particles on the sides of the vessel containing it. This idea was developed at greater length by Le Sage and Prevost,<sup>1</sup> by Herapath,<sup>2</sup> Joule,<sup>3</sup> and Krönig.<sup>4</sup> Joule, in fact, by very simple reasoning, arrived at the now recognised fact that the average velocity of the particles of hydrogen at 0°C. must be about 6055 feet per second. Clausius,<sup>5</sup> who has taken up this theory more in detail, considers a gas to be a collection of molecules always in motion, and deflecting each other from their courses only when at a very small distance from each other, so that the course of each molecule consists of a series of nearly rectilinear portions. The deflexions due to the encounters with other molecules are supposed to be so sudden that the encounters may be compared to collisions. He has determined the relation which exists among the following quantities:—the mean length of the path of a molecule between successive encounters, the distance of their centres at collision, and the number of molecules in unit of volume, and has shown that this theory is not inconsistent with any known

<sup>1</sup> *Deux Traités de Physique Mécanique*. Genève, 1818.

<sup>2</sup> *Mathematical Physics*. Whittaker & Co., 1847.

<sup>3</sup> *Some Remarks on Heat and the Constitution of Elastic Fluids*. Oct. 3, 1848. (See *Phil. Mag.* 1857, ii.)

<sup>4</sup> *Pogg. Ann.* 1856.

<sup>5</sup> *Phil. Mag.* Feb. 1859.

phenomena, provided we admit that the energy of each molecule consists partly of the motion of its centre of inertia, and partly of rotation or internal vibration, these two portions of the energy being on an average in a definite ratio depending on the nature of the molecules. This theory in the hands of Clausius explains the relations between the volume, temperature, and pressure of a gas, its cooling by expansion, and its two specific heats, together with the slowness of the diffusion of gases, and of the conduction of heat.

60. Clerk-Maxwell,<sup>1</sup> taking up the theory of Clausius, showed that it also led to the law, previously established by Gay-Lussac on chemical considerations, that if two gases have the same volume, pressure, and temperature, the *number* of their molecules is the same. He also applied the theory to explain the internal friction of gases, and endeavoured to estimate the probable length of the path described by a molecule between successive collisions. He was thus led to the conclusion that the viscosity of a gas is independent of its density, an unexpected result, which, however, was shown by Stokes to be deducible from the experiments of Graham<sup>2</sup> on the Transpiration of Gases.

Clausius,<sup>3</sup> in examining Maxwell's theory of the conduction of heat in a gas, pointed out some oversights in that theory, and improved and extended the method of investigation; and O. E. Meyer<sup>4</sup> investigated the viscosity of air, both experimentally, and as a mathematical consequence of the theory of elastic molecules.

61. Maxwell,<sup>5</sup> however, was induced by his own experiments<sup>6</sup> on the viscosity of air and other gases at different temperatures, and by the results obtained by Graham on transpiration, to substitute for the theory of elastic molecules, that of molecules repelling one another according to the

<sup>1</sup> *Phil. Mag.* 1860. Jan. and July.

<sup>2</sup> *Phil. Trans.* 1846.

<sup>3</sup> *Pogg. Ann.* Jan. 1862.

<sup>4</sup> *Pogg. Ann.* 1865.

<sup>5</sup> *Phil. Trans.* 1867.

<sup>6</sup> *Phil. Trans.* 1866.

inverse fifth power of the distance. He also succeeded, by means of this assumption, in simplifying the mathematical theory, and in adapting it to the cases of diffusion of gases, and conduction of heat in a gas, and in explaining the apparently anomalous results obtained by Graham relating to the viscosity of mixed gases.<sup>1</sup> The time has hardly yet come, however, in which much is to be expected from such hypotheses; we are as yet almost completely ignorant of the ultimate structure of the molecules or particles of matter, though the thoroughly satisfactory explanation<sup>2</sup> which the kinetic theory of gases furnishes of the motions of Crookes' *Radiometer* has recently supplied very strong additional arguments for the truth of that theory. The results of the dynamical theory of heat are, however, quite independent of particular assumptions like these as to the constitution of bodies.

62. Maxwell has obtained three results, which, though they are deduced from the theory of moving molecules, are independent of the mode in which these molecules are supposed to act on one another.

The first is the condition of equilibrium of energy between two sets of molecules of unequal mass, namely, that the energy of translation of a molecule of either kind must be the same. This is the dynamical expression of Gay-Lussac's Law of Equivalent Volumes.

The second is the condition of equilibrium of a vertical column of mixed gases, namely, that the density of each gas at any point is ultimately the same as if no other gas were present. This is the law laid down by Dalton as to the distribution of gases in equilibrium.

The third is the condition of equilibrium of temperature

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<sup>1</sup> The most recent experiments of Kundt and Warburg, however, seem to show that the viscosity increases according to a power of the absolute temperature which is different for different gases, but in no case exceeds 0.77.

<sup>2</sup> Dewar and Tait, *Proc. R.S.E.*, or *Nature*, July 1875. Stoney, *Phil. Mag.*, March and April 1876.

in a vertical column of gas, namely, that the temperature must be the same throughout, and it follows from this, by the dynamical theory of heat, that in *all* substances gravity has no effect in making the lower part permanently hotter or colder than the upper. These results have been confirmed by the elaborate investigations of Boltzmann.

63. A method of experimentally discovering, with very great accuracy, the relation between the heat produced and the work spent in the compression of a gas, was suggested by Thomson in 1851,<sup>1</sup> and employed with some modifications in a series of experiments, which he has since carried on in conjunction with Joule. Their results have been from time to time published in the *Philosophical Transactions* during the last twelve years, with the title *Thermal Effects of Fluids in Motion*. The principle of this method is excessively simple; it consists merely in forcing the gas to be experimented on through a porous plug, and observing its temperature on each side of the plug. These temperatures should (after the requisite corrections) be exactly equal if the heat developed by compression is equal to the work expended, and not otherwise. By this process it is found that no gas perfectly satisfies the criterion; and, as we might expect, the liquefiable gases are those which most diverge from it. By means of a sufficient series of such experiments, carried on at different temperatures and pressures, complete theoretical data for a gas-engine have been obtained; and the extensive and valuable experiments of Regnault (with additions, as to the density of steam at high pressures, derived by Joule and Thomson from their air experiments) have furnished corresponding data for the steam-engine; so that the theoretical treatment of these important instruments is now at all events approximately complete. But it is no part of the plan of this work to enter into details of *application*.

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<sup>1</sup> *Trans. R.S.E.*

64. A yet more important result, viz., that, to a very close approximation, Carnot's function (§ 26) is inversely as the temperature from the absolute zero measured on the air-thermometer (an idea first suggested by experiment to Joule, but which was assumed by others from mere hypothetical reasoning), was thus definitely introduced into science.

65. As already mentioned, the *direct* relation between heat and mechanical effect has alone been considered in the present chapter. The far more extensive results which have been arrived at with reference to *indirect* relations, and the consideration of the relations which have been proved to exist between heat and all other forms of energy will be taken up in Chapter II. What has been given is almost entirely confined to the thermo-elastic properties of liquids and gases. W. Thomson<sup>1</sup> has published an extremely general investigation of the laws of this subject, including crystalline solids; but to give a satisfactory account of it would involve details and difficulties far too great for any but a *very* small class of readers.

66. There remains, however, one interesting portion of the subject, which, though having most important bearings upon the subject of energy and its distribution through the universe, is in part a branch of Thermo-dynamics. This is the consideration, already alluded to, of the *Dissipation of Energy*.<sup>2</sup> But in accordance with the plan of the work, it must be considered at present only as regards heat and mechanical effect. In the first place, heat in a conducting body tends to a state of dissipation or diffusion, never to a *concentration* at one or more places. This is a direct consequence of the law of propagation of heat in a solid. Fourier's mathematical investigations point also to the fact that a uniform distribution of heat or a distribution tending

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<sup>1</sup> *Quarterly Math. Journal*, April 1855.

<sup>2</sup> *On a Universal Tendency in Nature to the Dissipation of Mechanical Energy*. By W. Thomson. *Proc. R.S.E.* 1852, and *Phil. Mag.* 1852, ii.



to become uniform, must have arisen from some primitive distribution of heat of a kind not capable of being produced by known laws from any previous distribution.<sup>1</sup> When Carnot's method, correctly adapted to the dynamical theory of heat, was applied by Thomson to the transformations of heat into work, and work into heat, it led him to the following amongst other propositions.

When heat is created by a reversible process, there is also transference, from a cold body to a hot one, of a quantity of heat, bearing to that created a definite ratio depending on the temperatures of the two bodies.

When heat is created by a non-reversible process (such as friction) there is a dissipation of energy, and a full restoration of it to its primitive condition is impossible.

From these it follows that any restoration of mechanical effect, from the state of heat, requires the using of more heat than the equivalent of the work obtained, this surplus going into a colder body. No further comment on this can be made at present, but in next chapter it will form a most important feature.

67. We have, as yet, said nothing of *Radiant* heat, of which the caloristic idea seems to have been exactly analogous to the Corpuscular Theory of Light. Davy actually speculates on the combinations of light and oxygen, in the very paper in which he destroyed the notion of the materiality of heat! The first really extensive, and on the whole trustworthy, experiments on radiant heat are those of Leslie, but we need not trouble ourselves with his theoretical speculations. The experiments of Forbes and Melloni showed so complete a resemblance between the laws of reflection, refraction, polarisation, absorption, etc., of light and radiant heat, that no doubt could remain as to their *identity*. And as light had, chiefly by the theoretical and experimental investigations of Young and Fresnel, been shown to consist in the undulations of some highly elastic

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<sup>1</sup> Thomson, *Cambridge Mathematical Journal*, 1843.

medium pervading all space ; it followed that radiant heat also is *energy* and not *matter*. Dark radiant heat differs from light merely as a grave note does from a shrill one. Light was shown by Leslie to heat bodies which absorb it, and on this principle he constructed his photometer. The paper of Mohr, already referred to (§ 30), contains, along with much error, many of the more obvious consequences of the establishment of the identity of light and radiant heat.

68. The law of exchanges, as it was called by Prevost, who first enuntiated it, explained what was erroneously called the radiation of cold, *i.e.* that a piece of ice brought near the bulb of a thermometer cooled it, with other more complex but perfectly analogous experimental results. He considered that all bodies radiate heat, but the more the higher is their temperature, so that, in the simple case above mentioned, the thermometer gave more heat to the ice than it received from it—a perfectly satisfactory explanation. This theory has since been greatly extended by Stewart, Kirchhoff, and De la Provostaye, who have independently arrived at the conclusion that the radiating power of a body for any definite ray of heat is equal to its absorbing power for the same. Light and radiant heat being identical, we may (with Melloni) speak of the *colours* of different kinds of radiant heat, and then the analogy, with corresponding phenomena in the case of light, becomes at once evident. A very curious example of the truth of this proposition, noticed by Stewart, is furnished by heating to whiteness a common earthenware plate, with a strongly-marked pattern, and looking at it in the dark, when we see, instead of a dark pattern on a white ground, a white pattern on a dark ground ; those parts which, when the plate is cold, appear dark, do so in consequence of their absorbing the incident light more freely than the white parts ; and when heated to whiteness, they appear bright because they radiate better. Stewart has also noticed, as another excellent proof, the fact that coloured glasses lose their colour in the fire.

De la Provostaye and Desains showed that, as most substances polarise (more or less completely) light reflected obliquely from their surfaces, so the light they radiate obliquely when heated to redness is partially polarised; but in the plane perpendicular to that of polarisation of the reflected rays. Kirchhoff and Stewart independently observed the beautiful phenomenon that the light radiated by a heated tourmaline plate (which polarises transmitted light) is polarised in the same plane as the light which the tourmaline absorbs. Kirchhoff derived from his investigation, and verified by conclusive experiments, the physical explanation of the production of the dark lines in the solar spectrum, which had, however, been previously suggested by Stokes, and of which Brewster had, long before, pointed out one of the causes, viz., the earth's atmosphere. The very amazing results of *spectrum analysis* cannot, however, properly be discussed here.

69. Kirchhoff's earliest publication<sup>1</sup> on this subject is of somewhat later date than that of Stewart, but it is more explicitly connected with the dynamical theory. The equality of radiation and absorption for every separate wave-length is here, for the first time, directly shown to be a consequence of the second law of thermodynamics. Also it is shown that as the temperature of a body becomes higher, not only does its radiation include rays of greater refrangibility, but the intensity of its radiation for *every* ray increases. Hence Kirchhoff is enabled to explain how it happens that a flame of *lower* temperature than the source is necessary for the production of absorption bands in the spectrum. Thus, for instance, in the spectrum of the Drummond or Oxy-hydrogen lime light no weakening of the double line *D* is produced by the interposition of a Bunsen gas-flame containing ignited sodium vapour; the radiation from the absorbing flame being sometimes more than sufficient to make up for the absorption. The light from the incandescent carbon points

<sup>1</sup> Berlin Academy, October, December, 1859. *Pogg. Ann.* 1860.

of the electric lamp, however, exhibits these lines strongly if passed through the Bunsen flame, even when a piece of metallic sodium burns fiercely in it. To produce the absorption bands in the spectrum of the Drummond light the comparatively cool flame of a spirit lamp (with salted wick) must be employed.

70. Stewart's<sup>1</sup> theoretical treatment of the subject is virtually based on the assumption (founded on experiment) that a thermometer placed within an enclosure formed of any materials and kept at a constant temperature, will finally assume that temperature, no matter by what screens the thermometer be surrounded. [This really involves, in one of its many forms, the second law of Thermodynamics.]

From this he shows, by very simple reasoning, that the absorption of a body at a given temperature must be equal to its radiation for every description of heat. He then experimentally proves that a plate of rock-salt, which absorbs little heat, radiates little. That both glass and rock-salt, cold, are more opaque to radiations from hot masses of their own substance than to radiations from any other body at the same temperature. And finally, that a thick plate of rock-salt radiates more than a thin one of the same temperature. From this last property he proves the existence of *internal radiation*, and shows that in non-crystalline bodies it is proportional to the square of the refractive index; a result also arrived at later, as a consequence of the second law of thermodynamics, by Clausius,<sup>2</sup> who employs a method analogous to that of Kirchhoff. It must be remarked, however, that this method of Kirchhoff's is merely a particular application of the splendid general investigations of Sir W. Rowan Hamilton.<sup>3</sup> Before the appearance of Kirchhoff's paper, Stewart had begun to

<sup>1</sup> *Trans. R.S.E.* 1858-9.

<sup>2</sup> *Pogg.* 1861, *Abhandlungen*, p. 322.

<sup>3</sup> *Theory of Systems of Rays* (1824). *Trans. R.I.A.* 1828, 30, 31, 37. *On a General Method in Dynamics.* *Phil. Trans.* 1834, 35.

extend his experiments to light, and had found, though not published, that a green glass when heated gives out reddish light and *vice versa*; and that a glass of any colour laid on glowing coals gives its own colour while colder than the coals, loses apparently all colour when it has acquired the temperature of the coals, and gives the complementary colour if hotter than the coals behind it.

71. The connection of the whole subject with the long-known proposition in geometrical optics that it is impossible by any series of reflections and refractions, to obtain an image brighter than the object, must be at once obvious.

72. Leslie's result, that a body, such as coloured glass, is heated by absorbing light, has recently received a most interesting extension from the discovery by Stokes<sup>1</sup> of the physical cause of certain curious phenomena observed by Brewster and Herschel, in solutions of quinine and certain kinds of fluor-spar, from the latter of which the phenomena have been called by the general name *Fluorescence*. The physical *fact* is simply this, that these and other bodies, especially the green colouring matter of leaves and 'canary' glass coloured with Oxide of Uranium, radiate as altered *light* part of the light which they absorb. This is, to a certain extent, analogous to Leslie's result, because the light radiated is lower in the scale than that absorbed, and is in general most freely produced from light so high in the scale as to be invisible to the eye (just as very shrill sounds, such as the chirp of the cricket, are inaudible to many ears). The most important application of this discovery has been to the rendering visible these invisible rays, and thus studying through a wider range of refrangibility the radiations from any source. The phenomena of *Phosphorescence*, when not traceable to chemical combination, evidently belong to the same class with those of fluorescence, and have been recently studied with great care by Becquerel, who has obtained many remarkable results. Another transforma-

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<sup>1</sup> *On the Change of the Refrangibility of Light.*—*Phil. Trans.* 1852.

tion of radiant heat, seemingly opposite in character to this, is *Calcescence* or *Calorescence*, where radiant heat from an intensely heated body, deprived of its luminous portion by absorption, and concentrated by a lens or mirror, produces incandescence even in incombustible bodies. This was predicted by Akin,<sup>1</sup> who described a process by which it might probably be obtained under very favourable circumstances ; but the experiment was first successfully performed by Tyndall.<sup>2</sup> The theory of this singular result is not yet quite clear, as it depends essentially upon an artificial arrangement producing extreme discontinuities of temperature. It is obviously connected with the fundamental principle of Kirchhoff's theory, (§ 69,) that a body when incandescent gives out a greater amount of dark heat than it does at any lower temperature.

73. Let us now, taking for granted the dynamical theory of heat, consider very briefly the explanations which it furnishes of many important phenomena, not alluded to in the preceding semi-historical sketch, because their explanation is very evident as soon as the true theory has been found.

74. Thus, for instance, Heat of Combination, as it is called, is obviously now to be explained as arising from the mechanical effect of the force of chemical affinity—whatever may be the nature and origin of that force—just as a stone falling to the ground under the action of the earth's attraction generates heat by the impact. From this explanation also follow as obvious truths, the laws of this subject, experimentally arrived at by Andrews, Hess, and others.

75. When a salt is deposited in crystals from a supersaturated solution, we have, in general, evolution of heat ; formerly this was attributed to the latent heat of solution, but it is now easily seen to be, like ordinary latent heat, dependent on the change of relative position of the mole-

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<sup>1</sup> *Brit. Ass. Reports*, 1863. *Phil. Mag.* 1864-5.

<sup>2</sup> *Phil. Mag.* and *Phil. Trans.* 1864-5.

cules involved. The contrary effect is of course produced when a salt is dissolved, and even when two crystalline solids, as ice and salt, liquefy in the act of combining. Hence the justice of the popular outcry against the common process of destroying ice on the pavements by sprinkling salt upon it; as, though the ice is melted, a great additional lowering of temperature is produced. Hence also the effect of the combinations called 'freezing mixtures,' which are of many kinds; from the simplest, such as the solution of nitrate of ammonia in water, to the most complex, such as the mixture of solid carbonic acid and ether *in vacuo*.

76. As was cursorily noticed at the commencement of this chapter, the so-called latent heat probably depends upon molecular arrangement; the heat, which is lost to the thermometer, disappears in producing, or is transformed into, the work of tearing asunder the particles of a solid or liquid, and placing them in the positions of less relative constraint which they occupy in a liquid or a vapour respectively. It is conceivable, however, that *it* also may be *motion*, but of a kind not tending to diffusion. But it is too early to speculate, with any prospect of useful results, on such a subject. We give, in the last chapter, a few remarks upon the speculations of Clausius.

77. The heat of the sun, and the internal heat of the earth—both of which, by the principle of dissipation, must be now far less than they were ages ago—are to be traced almost entirely to their origin in the primæval distribution of matter through space, at creation, and the subsequent transformation into heat of the energy with which the various portions which compose the sun or a planet impinged on each other in meeting.

But the consideration of such immense and important transformations must be deferred to the second chapter, where they will be found to flow naturally from the known laws of transformation and transference of energy.

78. Reviewing, for a moment, the path we have so far pursued, the successive steps, most important in a historical point of view, of the *foundation* and *development* (not the applications) of the science may be recapitulated. They are these :—

*First*, Newton's grand general statement of the laws of transference of mechanical energy from one body or system to another (1687).

*Second*, Davy's proof that heat is a form of energy subject to these laws (1799).

*Third*, Rumford's close approximation to a measure of the mechanical equivalent (1798).

*Fourth*, Fourier's great work on one form of dissipation of energy (1812).

*Fifth*, Carnot's fundamental principle, his cycles of operation, and his test of a perfect engine (1824).

*Sixth*, Thomson's introduction of an *absolute* Thermodynamic scale of thermometry (1848).

*Seventh*, Joule's exact determination of the mechanical equivalent of heat, and the general reception of the true theory in consequence of his *experiments* (1843-9).

*Eighth*, The adaptation, by Rankine and Clausius, and subsequently, with greater accuracy, generality, and freedom from hypothesis, by Thomson, of mathematical investigation (partly based on Carnot's methods) to the true theory ; the establishment of the second law by Thomson ; with Joule's experimental verification of Thomson's general results (1849-51).

*Ninth*, Thomson's theory of dissipation (1852).

As regards the true theory of the connection of heat with mechanical effect, this list contains all the most important direct steps, nearly in chronological order ; but it is to be remembered that experimental investigation, mainly due to Joule, has indissolubly connected by laws of equivalence *all* forms of energy, including even such mysterious forms as are observed in electro-chemistry and electro-magnetism ;



so that a complete account of the dynamical theory of heat necessarily involves, what we propose to give in the next chapter, an account of the grand law of natural philosophy known as the CONSERVATION OF ENERGY.

79. In the brief sketch above given, a vast amount of valuable matter has been of necessity omitted, but no direct step of real consequence to the development of the true theory of heat has been left unnoticed. Where the results of early experiments were sufficiently accurate, subsequent more perfect ones (such as the splendid series of researches by Régnault, and the valuable large-scale investigations of Hirn) have been merely alluded to ; and many curious, but not very important, points have not been mentioned. The details of such a history as this would fill volumes.

## CHAPTER II.

### HISTORICAL SKETCH OF THE SCIENCE OF ENERGY.

80. IN the preceding chapter the absurdity of attempting to base extensions of Natural Philosophy upon mere metaphysical speculations was very briefly considered ; and it was shown that without direct experimental proof, or the less direct but still conclusive proof furnished by rigorous mathematical deductions from experimental results, nothing can with any show of reason be predicated of the laws of Nature. Experience is our only guide in these investigations, for there can evidently be no *à priori* reason (to our intelligence)<sup>1</sup> why matter should be subject to one set of laws rather than another, so long at least as each of these codes is consistent with itself. The caloric or material theory of heat was particularly instanced as not only unjustifiable in itself, but (while it was received) antagonistic to all real progress. The corpuscular, or material, theory of light furnishes another excellent example. The preposterous nonsense which was gravely enuntiated, and greedily accepted, with regard to the nature and laws of light, and the elaborately absurd properties assigned to its supposed particles in order to fit them for their every-day work, would be almost inconceivable to a modern reader, were it not that equally, or even more, extravagant dicta of the 'great inexperienced' have been, and are even now being,

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<sup>1</sup> See ' *Herbert Spencer versus Thomson and Tait* '—*Nature*, March 26, 1874.

propounded by self-constituted interpreters of the original designs of Nature. Look at the dictum of the antient philosophers, who accounted for the planetary motions by saying 'circular motion is perfect.' Or, to come to modern times, let us see how the gigantic intellect of a Hegel can annihilate the conclusions even of Newton. 'The motion of the heavenly bodies is not a being pulled this way and that, as is imagined. They go along, as the antients said, like blessed gods. The celestial conformity is not such a one as has the principle of rest or motion external to itself. It is not right to say, because a stone is inert, and the whole earth consists of stones, and the other heavenly bodies are of the same nature as the earth, therefore the heavenly bodies are inert. This conclusion makes the properties of the whole the same as those of the part. Impulse, pressure, resistance, friction, pulling, and the like, are valid only for other than celestial matter.'<sup>1</sup> We nowhere find these preposterous dicta more prevalent, or more pernicious, than in the history of the grand question which we are about to discuss. We have no more reason, before experiment settles the question, to fancy Energy indestructible than the Calorists had for believing in the materiality of heat. The philosophers who said that '*Nature abhors a vacuum*' had at least an experimental basis for their guidance; and, if they had limited the generality of their statement to the class of circumstances really involved in their experiments, we might have smiled at the peculiarity of the language in which their conclusion was expressed, but we must have allowed their meaning to be correct.

81. But when we find, in modern times, conclusions, however able, drawn without experiment from such a text as '*Causa æquat effectum*,' we feel that the writer and his supporters are, as regards method, little in advance of the

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<sup>1</sup> See Whewell *On Hegel's Criticism of Newton's Principia*. *Camb. Phil. Trans.* 1849.

science of the dark ages. This is one of the fundamental characteristics of all the writings of Mayer,<sup>1</sup> and therefore we may for the present leave them unnoticed, although we shall afterwards have occasion to consider them as furnishing a most admirable development of the consequences of an unwarranted assumption. For, while there can be no doubt that the works of Mayer contain highly original and profound deductions from his premises, deductions of a most important character as regards the system of the universe, it is certain that those premises were unjustified by experiment, and therefore that his method was not merely unphilosophic but even inconsistent with true science.

82. Let it not be imagined that we undervalue the assistance which science often receives from what appear at first to be the wildest speculations—*so long as these are not elaborately enuntiated as a priori laws, but are confined to their only legitimate use, the suggestion of new methods of interrogating nature by experiment.* By all means let philosophic minds indulge in any vagaries they may choose to foster, but *let these be carefully distinguished from facts established by experiment*, and let them be kept as private magazines from which, when required, may be extracted an idea leading to an experimental research. In perhaps one case in a million, the expected result may follow: but, in the many cases in which it does not occur, there are thousands of chances (which will not be lost to the careful experimenter) of discovering something utterly unlooked for. Instances of this without number may be given. The discovery of electro-magnetism by Örsted was arrived at by his fancy that a conducting wire might when *heated* by

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<sup>1</sup> *Bemerkungen über die Kräfte der unbelebten Natur.*—Liebig's *Annalen*, 1842. *Die organische Bewegung in ihrem Zusammenhange mit dem Stoffwechsel*, Heilbronn, 1845. *Beiträge zur Dynamik des Himmels*, Heilbronn, 1848. Republished in a collected form, with the title *Die Mechanik der Wärme*, Stuttgart, 1867.

an electric current act on a magnet. Kepler's Laws were deduced by means of an almost incredible amount of numerical calculation based upon the supposition of the existence of all sorts of harmonies, perfect solids, etc. etc., in the solar system. In chemistry this mode of procedure has been long recognised as leading to most important results, since, in the attempt to produce directly some particular compound, it often happens that the experimenter is gratified by the appearance of some other which he had never dreamt of as capable of existing, or at least of being obtainable by his process. Mayer, therefore, and others who have followed a course similar to his, cannot be considered as having any claims to the credit of securely *founding* the science of Energy; though their works have become of great value as developments and applications, since the science has been based upon correct reasoning and rigorous experiments.

83. Particular cases of the Conservation of Energy were experimentally discovered, but without any reference to the great principle, at early stages of the progress of electricity, electro-chemistry, heat of combination, and various other branches of science; and many curious cases of Transformation and Dissipation of Energy had also been observed. To these we shall advert after we have given a brief sketch of the Laws of Energy and the history of their discovery; as we shall then be enabled to classify them properly, and to show their mutual connection.

84. Before entering upon the history of this development, we may premise a few words on *Dynamical Theories in General*.

An exact Science is one the nature and connection of whose phenomena may be expressed in exact terms.

A dynamical theory of a science is one which explains its phenomena by the existence of bodies acting on one another with determinate forces, and moving in a determinate manner. A theory which ascribes to these bodies, forces, or motions any qualities differing from those of the bodies,

forces, and motions treated of in pure dynamics is not a dynamical theory.

A dynamical theory consists of four parts.

The first part considers the possible motions of the system without reference to the forces producing them. This is called *Kinematics*.

The second considers in what cases one system of forces is equivalent to another. If one of these systems is reversed, the whole will be in equilibrium. Hence this investigation has been called *Statics*. It is independent of the nature of the bodies on which the forces act.

The third part treats of the effect of forces on the motions of material bodies. This may be called *Kinetics*.

The fourth part considers the conditions under which forces act between the different parts of the system, and thus transmit energy from one part to another. This may be called *Energetics*.

85. In some departments of physical science we have ascertained the energy required to produce certain effects, without being able to measure on any sound principle either the magnitude of the effect, or the force required to produce it.

In ordinary kinetics, the effect is sometimes measured as the number of feet through which the resistance is overcome; the resistance expressed in pounds weight is the other factor, if the energy is expressed in foot-pounds.

In hydrostatics, when a fluid is forced into a vessel, the volume of the fluid, and the pressure at which it is forced in, are the factors of the energy.

In the transfer of electricity, the quantity transferred, and the electromotive force opposing the transfer, are the factors.

But in chemistry, though the total energy let loose during the combination of two given substances can be ascertained in many cases from the heat produced, the measurement of the force which produces this effect has not been so clearly understood. To measure this force in pounds weight, it

would be necessary to know the distance between the combining molecules at every stage of the combination, and for this we have no data whatever. W. Thomson, however, in his *Mechanical Theory of Electrolysis*, has given a method by which in many cases the force of 'chemical affinity,' so much studied in former times, and so neglected now, may be expressed in a perfectly definite measure. This measure is that of electromotive force, and the numerical value of the electromotive force which expresses the resultant chemical affinity involved in a given reaction is equal to the mechanical value of the whole heat evolved during this reaction, when *one* electro-chemical equivalent of each substance enters into the combination.<sup>1</sup>

Thomson has also done a service of primary importance to the corresponding part of thermodynamics. The condition of the transfer of energy from *A* to *B* depends on the relative value of  $\alpha$  and  $\beta$ , where  $\alpha$  and  $\beta$  are functions of the state of *A* and *B*. If *A* and *B* are vessels containing fluid, and put in communication, then  $\alpha$  and  $\beta$  are the pressures in these vessels, and the value of  $\alpha - \beta$  determines the direction and force of the transfer of fluid. If *A* and *B* are electrified,  $\alpha$  and  $\beta$  will be their potentials. If *A* and *B* are hot bodies,  $\alpha$  and  $\beta$  will be their temperatures. Temperature, therefore, as has long been understood, is a quantity which determines whether a body shall part with its heat to other bodies, and temperature as measured by any particular thermometer is a quantity which satisfies this condition. But in the ordinary measure of temperature, though we may assert that the temperature of *A* is greater or less than that of *B*, we cannot assert that the temperature of *A* exceeds that of *B* as much as the temperature of *C* exceeds that of *D*, merely because the differences measured in degrees of our thermometer are the same, for one thermometric sub-

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<sup>1</sup> See Clerk-Maxwell and Jenkin on Elementary Relations between Electrical Measurements, *Brit. Ass. Report*, 1863, Art. 54.

stance differs from another in its law of expansion. By the establishment of an absolute scale of temperature (§ 26), however, we may treat differences of temperature with the same mathematical completeness as differences of pressure or of potential.

86. In order that the reader may understand clearly the terms which it is essential to employ in giving a strictly accurate, although popular, view of the laws of Energy, it will be useful to give preliminary examples of various forms of energy constantly presenting themselves to his notice. Let us consider, for instance, gunpowder. It contains, in a dormant form, an immense store of energy, or, in common mechanical language, it can do an immense amount of *work*. Its use in blasting is simply to do at little expense, and in a short time, an amount of work which it would take many labourers a considerable time to perform. In virtue of the arrangement of its chemical constituents it possesses, in a small compass, this store of work-producing power. Again, in order that water in a reservoir may be capable of supplying motive power to mills or other machinery, it must be capable of descending from a higher to a lower level, for no work can be got out of still water, unless it have a *head* as it is technically called. When the driving-weight of a clock has run down, the clock stops ; and in order that the weight may be rendered again efficient in maintaining the motion of the wheels and pendulum, it must be wound up, or placed in such a position, relatively to the earth, that work can be got out of it in consequence of that position. In an air-gun we have a store of energy laid up in the form of compressed air ; in a cross-bow, a wound-up watch, or the lock of a cocked gun—in the form of a bent spring ; in a charged Leyden jar—in the form of a distribution of electricity ; in a voltaic battery—in the arrangement of chemical elements or compounds ; in a labourer, primed for work—in the form of a proper supply of food. In all such cases, where the energy is dormant, it is called *Poten-*



*tial Energy*,<sup>1</sup> and its amount is measured by the work which it is capable of doing, and which it will do if properly applied.

87. The unit for measurement of work usually employed by British engineers is the foot-pound; and though this varies in amount from one locality to another, it is in such general use, and so convenient when absolute accuracy is not required, that it will be employed throughout this chapter. It is the amount of work required to raise a pound a foot high. It is evident that to raise any mass to a given height, the amount of work required is proportional to the number of pounds in the mass, and also to the number of feet through which it is to be raised. Thus to raise a cwt. a furlong high requires the same expenditure of work (73,920 foot-pounds) as to raise a stone-weight a mile high, or a pound 14 miles. And the potential energy of the raised mass, or the work which can be got out of it in virtue of its position, is precisely equivalent to the work which has been employed in raising it.

[The French or metrical unit of work is one kilogramme raised through one mètre in the latitude of Paris; and is called a kilogrammètre. Neglecting the dependence of gravity upon latitude, the value of a kilogrammètre is 7·2331, or a little less than seven and a quarter, foot-pounds.]

88. But if the mass be allowed to fall, we may remark that it gains velocity as it descends, and that the square of the velocity acquired at any point of the path is proportional to the space through which the mass has fallen. Also when a projectile is discharged vertically upwards it possesses no potential energy at the commencement of its flight, but it has, *in virtue of its motion*, energy, or power of

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<sup>1</sup> The term *Energy* is due to Young, *Potential Energy* to Rankine. The idea of Potential Energy seems to have been first distinguished by L. N. M. Carnot, who speaks of *force vive latente* (*Principes . . . de l'Equilibre et du Mouvement*, Paris, 1803), and by W. Thomson, who called it *Statical Energy*.

doing work. To measure this energy, we must find how much work it is capable of producing, and we find that it is proportional to the *square* of the velocity. That is, a projectile discharged upwards will rise to four times the height if its initial velocity be doubled, to nine times if trebled, and so on. If we now introduce the term *Kinetic*<sup>1</sup> *Energy* to signify the amount of work which a mass can do in virtue of its motion, we must measure it by half the product of the mass into the square of its velocity; and the ordinary formulæ for the motion of a projectile show that, neglecting the resistance of the air, the sum of the Potential and Kinetic Energies remains constant during the flight. There is perpetual transformation of kinetic into potential energy, as the projectile rises, and a retransformation as it descends.

89. An excellent illustration is furnished by the simple case of the oscillation of a pendulum, where the energy originally given to the bob, either in a kinetic form by projecting it from its lowest position, or in a potential form by drawing it aside from the vertical, and then letting it fall, is constantly transformed and retransformed every quarter oscillation.

90. The observations above made on these very simple cases are found to be completely borne out in more complex ones, as, for instance, in the oscillations of an elastic body, such as the balance-spring of a watch, a tuning-fork, etc. Here the potential energy consists in a deformation of the elastic body, as in bending a spring, etc. etc. All this, however, is on the supposition that the bodies are perfectly elastic, and that there is no external resistance to the motion.

91. The complete theory of all such cases was enuntiated in a perfect form by Newton in the *Principia* as a scholium to his Third Law of Motion; in which he not only laid down the so-called Principle of Vis-Viva, and D'Alembert's Prin-

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<sup>1</sup> 'Energy,' by Thomson and Tait—*Good Words*, 1862.

ciple, for which others long afterwards obtained great credit; but stated, so far as the development of experimental science in his time permitted, the great law of Conservation of Energy. This remarkable passage appears, until lately, to have escaped notice; or, at least, not to have received sufficient consideration. It is as follows:—

*‘Si æstimetur agentis actio ex ejus vi et velocitate conjunctim; et similiter resistentis reactio æstimetur conjunctim ex ejus partium singularum velocitatibus et viribus resistendi ab earum attritione, cohæsione, pondere, et acceleratione oriundis; erunt actio et reactio, in omni instrumentorum usu, sibi invicem semper æquales.’*

By the context it is easy to see that the *actio* here spoken of by Newton is precisely what is now called *rate of doing work*, or *horse-power*. Also the *reactio*, as far as acceleration is concerned, is precisely what is now known as *rate of increase of kinetic energy*. Newton’s statement is therefore, in modern phraseology, equivalent to this:—

*Work done on any system of bodies has its equivalent in the form of work done against friction, molecular forces, or gravity, if there be no acceleration; but if there be acceleration, part of the work is expended in overcoming resistance to acceleration, and the additional kinetic energy developed is equivalent to the work so spent.*

As we have already seen, when part of the work is done against gravity, as in raising a weight, or against molecular forces, as in bending a spring, it is stored up as potential energy; and the recoil of the spring, or the fall of the weight, are capable at any future time of restoring the work expended in producing these effects. But in Newton’s time, and long afterwards, it was supposed that work spent in friction was *absolutely lost*. Now, by the experimental researches of Davy, Rumford, and Joule, we know that it is merely transformed into other and more inscrutable, but equivalent, quantities of energy in the forms of heat and electrification or electric motion.

92. But, before passing to these higher considerations, it may be well to exemplify Newton's great discovery, by applying it to such common cases of transformation of energy as have been already mentioned, or are constantly observed, and which are not much influenced by the production of heat or electricity. Thus, in the case of the simple pendulum, when it is at one end of its range, it has potential energy, in virtue of which work can be done upon it by gravity. This is wholly expended in producing acceleration of motion as the bob descends; and, when it has reached its lowest position, the kinetic energy produced is equivalent to the work so done, that is, to the potential energy lost. As it rises again, work is done against gravity, which is stored up as potential energy; but the work so done comes from the store of kinetic energy possessed by the bob; and when this is exhausted, the bob rests for an instant, to pursue a similar course of transformations. With the change of a word or two, the same explanation applies to the oscillations of the balance-spring of a watch. In the case of a tuning-fork, however, the oscillations more rapidly diminish in energy; but here we have still the law of conservation, because part is by imperfect elasticity changed into heat within the substance of the fork, and what is lost to the fork is communicated to the air, becoming transformed into the kinetic energy of sound. Its ultimate fate will occupy us presently.

93. The leading dates in the history of the *foundation* (not the *development*) of the science of energy, besides those given in the preceding chapter, are few and comparatively definite.<sup>1</sup>

In January 1843,<sup>2</sup> Joule showed that mechanical work can be converted into an equivalent of heat mediately by the induced currents of the magneto-electric machine, and thus that current electricity is a form of energy subject to

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<sup>1</sup> See Tait, *Recent Advances in Physical Science*.

<sup>2</sup> *Memoirs of the Lit. and Phil. Soc. Manchester*, vol. vii.

the law of conservation. This step enabled him to apply his previous investigations (whose publication dates from 1840) regarding electrolysis to the establishment of the principle of energy in chemical action. Thus, to quote only a few sentences, he says—

‘However we arrange the voltaic apparatus, and whatever cells of electrolysis we include in the circuit, the whole caloric of the circuit is exactly accounted for by the whole of the chemical changes.’

‘The mechanical and heating powers of a current are proportional to each other.’

‘I have little doubt that by interposing an electro-magnetic engine in the circuit of a battery, a diminution of the heat evolved per equivalent of chemical change would be the consequence, and in proportion to the mechanical power obtained.’

94. In August 1843, Joule read to the British Association, at Cork, a paper entitled ‘*On the Calorific Effects of Magneto-Electricity, and the Mechanical Value of Heat.*’ This was inserted in the *Philosophical Magazine*, in October and succeeding months of the same year. The main object of the paper is the determination of the mechanical equivalent of heat by causing a small electro-magnetic arrangement to revolve between the poles of a larger electro-magnet, and measuring the heat developed in the smaller coil after the expenditure of a known amount of work in turning it. He displayed great resources as an experimenter in deducing from this combination results, which, considering the extreme difficulty of the process, agreed wonderfully well with each other, and which led to a mean value (838 foot-pounds) of the dynamical equivalent of heat (only)  $8\frac{1}{2}$  per cent. too high. He has shown that some error was to be expected from the impossibility of measuring, and taking account of, the fraction of the whole heat developed, which fell to the share of the large electro-magnet. But he carefully proved that heat is developed in the *whole* circuit, and that it is not merely transferred by induction from one part of the circuit to another: thus supplying an additional proof to that of Davy, of the immateriality of heat. This

experiment has since been converted by Foucault and others into a very striking lecture-room illustration of the transformation of work into heat.

The appendix to this paper contains the wonderful approximation (770 foot-pounds) to the value of the dynamical equivalent of heat deduced by friction of water, which was examined in the preceding chapter.

95. Thus, in all the scientifically legitimate steps which the early history of the principle records, Joule had the priority. His work has been much extended by others, especially Clausius, Helmholtz, Mayer, Rankine, and Thomson, in the developed applications of the principle in many directions. To their results the reader's attention will presently be directed; but he should clearly recognise the fact that the experimental foundation of the principle in its generality, and the earliest suggestions of many of its most important applications, belong unquestionably to Joule. Trained to accurate experiment and profound reflection in the school of Dalton, the pupil has not only immortalised himself, but has added to the fame of the master.

96. In an admirable tract by Helmholtz<sup>1</sup> (who must be classed as one of the most successful of the early promoters of the science of energy on legitimate principles), the whole subject is based upon Newton's principle, with one or other of the following postulates:—

(a) Matter consists of ultimate particles which exert upon each other forces whose directions are those of the lines joining each pair of particles, and whose magnitudes depend solely on the distances between the particles.

(b) 'The Perpetual Motion' is impossible.

This is, of course, a strictly logical foundation for the science of Energy, if it be taken for granted *as an experimental result* that the perpetual motion is impossible; or if

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<sup>1</sup> *Ueber die Erhaltung der Kraft*—Berlin, 1847. Translated in *Taylor's Scientific Memoirs*, 1853.

we could be sure that the ultimate parts of matter act on each other in the manner assumed. Unfortunately, it must be confessed that we know nothing as to the ultimate nature of matter, and (a) is not in the present state of experimental science more than a very improbable hypothesis. Again, to assume (b) is apparently to beg the question, to assume in fact that the Conservation of Energy applies not only to such cases as Newton had already treated, but to the more mysterious actions of heat, electricity, etc.<sup>1</sup> And though Joule's experiments have shown that even for these the principle holds good: there is, it is to be feared, still a fond hope entertained by many that the perpetual motion may perhaps yet be obtained by electrical processes. This has received a sort of countenance from the fact, that the best-known complete hypothesis (that of Weber) on which the mutual actions of electric currents have yet been explained, requires the admission of mutual forces between moving quantities of electricity, which are *not* consistent with (a).<sup>2</sup> But before the *facts* discovered

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<sup>1</sup> That Helmholtz, even in 1847, five years after Mayer's paper (which is by some said to have settled the question) appeared, regarded the inquiry as a merely speculative one, on which experiment alone could decide, is evident from his remark: 'In den Fällen, wo die moleculären Aenderungen und die Electricitätsentwicklung möglichst vermieden sind, würde sich diese Frage so stellen, ob für einen gewissen Verlust an mechanischer Kraft jedesmal eine bestimmte Quantität Wärme entsteht, und inwiefern eine Wärmequantität einem Aequivalent mechanischer Kraft entsprechen kann.'

<sup>2</sup> In *Poggendorff's Annalen*, 1848, vol. 73, Weber pointed out that his very remarkable law of electric attraction does give a potential—in the sense that the electric force in any direction upon a particle of electricity is the rate of diminution, per unit of length in that direction, of a certain function. It follows that when the system has been brought back to its original configuration and its original velocities, no work on the whole has been done. Clerk-Maxwell has shown that it is on this account that Weber's Theory is consistent with the production of induced currents. But this potential involves *relative velocities* as well as relative positions, and cannot therefore be properly

by Joule, all such objections must give way; just as the corpuscular theory of light, even if we had not had the undulatory theory to take its place, must have at once been abandoned when it was found that light moves faster in air than in water. Our real difficulty in such a case as this is not with regard to the truth of the Conservation of Energy, but with regard to the *nature of electricity*; and Weber's result merely shows that electricity does not consist of two sets of particles, vitreous and resinous, not that there is a loop-hole for escape from the grand law of Energy. Such a digression as this is not without its use, if it give any reader a more complete idea of the nature of the difficulties with which science is at present most encumbered; that they consist more in our ignorance of the nature of matter and energy than of the grand laws to which their actions are ultimately subject.

97. The Theory of Energy, as at present developed, contemplates its Conservation, Transformation, and Dissipation.

The principle of *Conservation of Energy* asserts that the whole amount of energy in the universe, or in any limited system which does not receive energy from without, or part with it to external matter, is invariable.

The *Transformation of Energy* is the enunciation of the experimental fact, that in general any one form of energy may by suitable processes be transformed, wholly or in part, to an equivalent amount in any other given form.<sup>1</sup> It is

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called potential energy. Weber's formula has been very ably discussed by Helmholtz in *Crelle's Journal*, but to give an idea of his reasoning requires higher mathematics than I can venture to introduce in this volume. I may merely mention that he shows that Weber's result is in certain cases inconsistent with electric equilibrium.

<sup>1</sup> Under the title *Correlation of the Physical Forces*, a great many of these transformations of energy were discussed by Grove in 1842, and he has since published a very curious work on the subject. Mrs. Somerville in 1834, in her work '*On the Connection of the Physical Sciences*,' seems to have been among the first to call attention to the generality of such transformations.



subject, however, to laws analogous to, and including, that of Carnot, and to limitations which are supplied by

The *Dissipation of Energy*. No known natural process is exactly reversible, and whenever an attempt is made to transform and retransform energy by an imperfect process, part of the energy is necessarily transformed into heat and *dissipated*, so that it cannot be wholly retransformed into energy of visible motion of bodies. It therefore follows, that as energy is constantly in a state of transformation, there is a constant degradation of energy to the final unavailable form of uniformly diffused heat; and that this will go on as long as transformations occur, until the whole energy of the universe has taken this final form.<sup>1</sup>

98. The remainder of the chapter will be devoted to a semi-historical enumeration of cases occurring in nature or experiment, and exemplification of the above laws in the circumstances of each case.

99. The simplest cases are, of course, those of abstract dynamics; when we consider motion of a material system under the action of any forces, but unresisted by friction. The pendulum, balance-spring, projectiles, etc., have already been noticed. As another instance, we may refer to the motion of a planet about the sun. When in perihelion, that is, when its potential energy is least, its velocity, and therefore its kinetic energy, is greatest. In the case of a comet moving in a parabolic orbit, the whole energy at any time is equal to the potential energy at an infinite distance from the sun; and thus as the comet recedes from the sun, the velocity, and with it the kinetic energy, become less and less, tending ultimately to zero. That a cannon ball, fired horizontally *in vacuo*, may just rotate about the earth, its velocity must be such as it would acquire by falling under

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<sup>1</sup> Thomson '*On a Universal Tendency in Nature to the Dissipation of Mechanical Energy*.'—*Proc. Royal Soc. Edin., and Phil. Mag.*, 1852.

the action of ordinary terrestrial gravity (at the surface) through a space equal to half the earth's radius; about five miles per second. In this case it would complete a revolution in about 85 minutes, or the seventeenth part of 24 hours.

100. In all these cases the potential energy involved, whether it depend upon molecular forces, as in a spring, or upon external forces, as gravity, is of the same species as that of a raised weight; and the only form of kinetic energy contemplated is that of visible motion. And here there is constant transformation from one of these forms to the other, and back again, for ever, without loss by dissipation, as the process is in each case exactly reversible. They give us, therefore, little insight into the more complex phenomena to which we proceed. They are all summed up in the law of conservation of *Vis Viva*, which we have already seen to be merely a different form of statement of one of Newton's discoveries. But in the ordinary text-books, the *loss of vis viva* in the impact of imperfectly elastic bodies is asserted, and its amount calculated; not a hint being given that the so-called loss is merely a transformation, partly, no doubt, into the potential form of distortion of the impinging bodies, but mainly into the kinetic form—heat. The same text-books also assert that there is no loss of *vis viva* in the impact of perfectly elastic bodies. This is, of course, true, but *not* in the sense in which it is asserted, since in the case of impact of perfectly elastic bodies, a portion of the *vis viva* of each would be changed, in general, into vibrations of the body itself, and would, therefore, not appear as part of the *vis viva* of the body considered as moving as a whole. Take, for instance, the case of a bell and its clapper, both supposed perfectly elastic.

101. As an example of the simpler cases of the loss by friction, we may consider the experiment originally suggested by Rumford, tried in a very imperfect manner by Mayer, and completely worked out by Joule. When a mass of

water in an open vessel is made to rotate by stirring, its free surface assumes a paraboloidal form; and therefore the energy communicated to it is partly kinetic and partly potential, the latter being a temporary transformation of a portion of the former. But, if it be left to itself for a short time, it comes to rest with its surface horizontal, so that both of these forms of energy have disappeared; and the water is, in all respects, except its temperature and the effects depending thereon, precisely as it was before stirring. Hence, if it be allowed to communicate its excess of temperature to surrounding bodies, it will remain precisely as before the operation, and by Carnot's axiom we are entitled to regard the heat it has given out as the exact equivalent of the work spent upon it. But the results of this process were detailed in the preceding chapter. As another illustration we may state, that when we see water flowing silently and unaccelerated down the bed of a stream, the potential energy is by fluid friction transformed into an increase of the temperature of the water, and thus wasted, so far as regards the production of useful work.

102. Sound has been already alluded to as the form in which part of the energy of a tuning-fork is wasted. Sound consists in fact of a state of air precisely analogous to the state of the matter of the vibrating fork; comprising a certain amount of potential energy in the form of compression or dilatation of air, analogous to the strain in the distorted steel; and a complementary amount of kinetic energy in the vibrations of the particles of air. If air had no viscosity, the transference of energy to it from the fork would be simply a case of impact, easily reduced to a question of abstract dynamics; and the energy so transferred would be propagated without loss in a form partly potential and partly kinetic, in spherical waves through the atmosphere. The energy of a complete wave in any such hypothetical case is, curiously enough, always equally divided between the two forms: and since, as the wave spreads, the amount of energy

in a given volume of air must be inversely proportional to the whole volume of air occupied by the wave, the intensity diminishes inversely as the square of the distance from the centre of disturbance. There is, of course, in the portion of the wave where the air is condensed, a rise of temperature, but in the rarefaction of the air in the other half of the wave, an equivalent fall of temperature occurs; so that, to a first approximation, the mean temperature is unchanged by the disturbance. But, in the actual case, the viscosity of the air due to fluid friction is constantly converting a portion of the energy of the wave into heat by an irreversible process, and therefore the intensity of sound diminishes more rapidly than the law of the inverse square of the distance (which may hold, so far as experiments have yet shown, for light and radiant heat in the interstellar space) would require, its energy being constantly wasted in raising the mean temperature of the air.<sup>1</sup> All motions of air, whether sounds or winds, therefore, are ultimately transformed into heat, and thus dissipated and lost, though not destroyed. Whether there is anything analogous to this in the case of undulatory motions in the inter-planetary ether is a grand, but as yet almost entirely unattempted, inquiry.

103. But in actual experience the results of even the simplest theoretical cases of abstract dynamics are never realised. For, besides the friction between solids, and the viscosity of fluids just considered, every motion of matter is resisted by the all-pervading ether;<sup>2</sup> and, on account of the generation of electric currents, which in their turn become heat, there is, in general, resistance to motion of conducting matter in a magnetic field. The consideration of these more recondite effects will be entered upon a little

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<sup>1</sup> Stokes on the '*Internal Friction of Fluids in Motion.*'—*Camb. Phil. Trans.* 1845. See also *Phil. Mag.*, 1851, i. p. 305.

<sup>2</sup> Stewart and Tait, '*On the Heating of a Disc by Rapid Rotation in Vacuo.*'—*Proc. R. S.* 1865-6.

later ; but we will endeavour to render the transition as gradual as possible.

104. We will now, partly following Helmholtz, consider in order the application of the laws of § 97 to the various forms of physical energy in the more common cases which have not as yet been particularly referred to, merely mentioning that he commences with a brief sketch of the applications (already given above) of Newton's principle to cases of abstract dynamics. Among these is one which we have not yet noticed, viz., that Fresnel, in deducing hypothetically the laws of polarisation of light by reflection and refraction, made the conservation of Vis Viva the foundation of his investigations, and arrived at results which are at least very close approximations to truth.

105. The *direct* relations between mechanical energy and heat have been sufficiently considered in the preceding chapter, and they are therefore merely alluded to here in order to maintain the continuity of the sketch. The *indirect* relations between energy of all kinds and heat will appear continually in the applications which follow.

106. We now pass to the consideration of the bearing of the laws of energy upon the production of ordinary (so-called) frictional electrification. There are two common methods by which electrification of high tension is *directly* produced, viz., by the ordinary electric machine, and by the electrophorus.

107. When *any* two bodies of different kinds are brought into contact, there is a certain amount of exhaustion of the potential energy of chemical affinity between them (similar to that of water which has reached a lower, from a higher, level) and the equivalent of this is, partly at least (for it is not yet known how bodies having chemical affinity attract each other at a distance), developed in the new potential form of a separation of the so-called electric fluids ; one of the bodies receiving a positive, and the other an equal negative, charge. The quantity of electricity, so developed,

depends upon the nature and the form of the bodies : and is determined by the simple law (whose terms will be presently explained), that the difference of electric potentials in the two bodies, if they be conductors, and possibly in the parts in contact, if they be non-conductors, depends only on the nature of the bodies.

108. So long as the bodies remain in contact, it is impossible to collect from them any of this electricity by means of metallic conductors ; but since, in virtue of their opposite charges, the bodies attract each other more than before, more work has to be employed in separating them than was gained in allowing them to come together. The equivalent of the excess of work appears in the mutual potential energy of the separated electricities. This is, in all probability, the source of the electricity usually ascribed to friction : so that the extra work required to turn an electric machine when in good order, supposing the true friction the same, would be (speaking roughly, and making no allowance for sparks, noise, production of ozone, etc.) directly as the square of the quantity of electricity produced. The machine, therefore, acts by contact of dissimilar bodies, producing a separation of electricities, and the application of mechanical energy so as to tear these farther asunder. And it is probable that all friction, perhaps not excepting that caused by actual abrasion, is due to the production of electricity.<sup>1</sup>

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<sup>1</sup> Thomson (*Bakerian Lecture*, 1856, *Phil. Trans.*, footnote to second page) says, 'It appears highly probable that the first effect of the force by which one solid is made to slide upon another, is electricity set into a state of motion ; that this electric motion subsides wholly into heat in most cases, either close to its origin and instantaneously, as when the solids are both of metal ; or at sensible distances from the actual locality of friction, and during appreciable intervals of time, as when the substance of one or both the bodies is of low conducting power for electricity ; and that it only fails to produce the full equivalent in heat for the work spent in overcoming the friction, when the electric currents

109. The electrophorus gives us a good instance of the direct conversion of work into electric potential energy. When the metallic disc is lifted from the excited plate of resin, work requires to be expended to overcome the attraction of the electricity in the plate for the opposite electricity developed by induction in the disc; and the equivalent of this work appears as the potential energy of the electricity thus detached. Hence, when we charge a Leyden jar, whether by the ordinary machine or by the electrophorus, the energy of the charge is a transformation of the work expended by the operator.

110. The potential, at any point, of a distribution of electricity, is the work required to convey unit of positive electricity, against the electric repulsions, from an infinite distance to that point. From this definition it is evident that the difference of the potentials at any two points is the work required to carry unit of negative electricity from one to the other; and therefore, by the definition of work, *the attraction on unit of negative electricity at any point in any direction is the rate of increase of the potential at that point per unit of length in that direction.* Hence the potential must have the same value at all points of a conducting body, for otherwise there would be (at points where its value changed) a resultant electric force, which observation proves never to exist in the interior of a conductor. Thus the potential of any conductor is the work required to remove a unit of negative electricity from *any* point of its surface to an infinite distance; or, what is easily shown to be numerically equivalent to this, it is the amount of electricity which must be given to a sphere of unit-radius connected with the conductor by a long fine wire; so that there may be no tendency to transference of electricity along the wire.

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are partially diverted from closed circuits in the two bodies, and in the space between them, and are conducted away to produce other effects in other localities.'

111. For any solitary conductor, as it is obvious that a small and a large charge will be *similarly* distributed over it, the potential is proportional to the quantity of electricity in the charge. In fact the charge is the product of the potential into a quantity called the *capacity*, which depends upon the form and dimensions of the conductor, and its position relatively to other conductors. And it is easily seen that the potential energy of the charge is the work which would have to be expended in bringing the charge, by successive small instalments, from an infinite distance, to the surface of the conductor. Helmholtz showed that this is half the product of the charge and the potential; hence, as the potential is proportional to the charge, the potential energy is, *ceteris paribus*, proportional to the *square* of the charge. Helmholtz also showed that, if there be more than one conductor, the whole energy is half the sum of the products of the charge and potential of each.

112. A precisely similar process is applicable to such a conductor as a Leyden jar; and, in fact, to any statical distribution of electricity. We thus see how the law, discovered independently by Joule, Lenz and Jacobi, and Riess, that the heat evolved by an electric discharge depends, *ceteris paribus*, on the square of the quantity of electricity in the charge; or by Joule that, in voltaic electricity, it depends on the square of the quantity of the current; accords with the conservation of energy.

113. The result of § 111, with Green's law of the capacity of a jar, shows that in a jar of given material and form, and with a given charge, the potential energy is inversely as the surface of the jar, and also directly as the thickness of the glass. The former of these statements gives an instructive example of the dissipation of energy. Thus, if a charge be divided between two equal jars, by simultaneously connecting the pairs of outer and inner coatings, half of the charge passes from the one jar to the other, and in doing so generates heat, sound, and light, each of which corresponds to a



loss of energy. The whole amount of electricity still remains, but, being diffused over a greater surface, it has less energy than before in proportion to the diminished potential. Thus, with equal charges, and equal thickness of glass, a small jar will give a more powerful shock than a large one.

114. It has already been mentioned that contact of two bodies, such as zinc and copper, develops a constant difference of potential between them. From the explanations subsequently given with reference to the potential, we see that this is equivalent to saying that at the surface of contact of two metals there is perpetually a force tending to separate the two electricities in a direction perpendicular to that surface, while at points ever so little within either of the bodies there is no such force. The only way in which we can conceive this to take place is by supposing that the surfaces in contact are equally and oppositely electrified. The effect of such an arrangement of electricity is nil on points in either of the bodies, but at the surface of separation it accounts for the force to which is due the difference of potentials in passing from one body to the other. If this be the true explanation, it will follow, as Helmholtz has pointed out, that bodies differ from each other in the amount of the forces, *sensible only at insensible distances*, which they exert upon positive and negative electricity. By no fixed arrangement of *simple* conductors can a current of electricity be produced; in fact it is obvious that if such were the case, the current would continue for ever, constantly producing heat by the resistance to conduction, which is of course impossible.

115. By means, however, of a very simple arrangement, not involving electrolysis, Thomson<sup>1</sup> has shown how to collect the electricity developed in either of two metals in contact; but, as the principle of energy requires, mechanical

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<sup>1</sup> *Proc. R. S.* 1867. (*N. B. Rev.* 1864.)

energy has to be expended. He allows water, or copper filings, to drop from a copper can, the drops falling (without touching it) through a vertical zinc cylinder which is in metallic contact with the can. Each drop carries with it electricity induced by electrostatic induction in the air between the zinc and copper : and, if they be collected in an insulated dish, the latter may be charged to any extent. The apparatus is, in fact, an electrical machine worked by gravity ; and the energy of the charge acquired by the insulated body on which the drops fall is accounted for by a deficiency in the heat produced by their impacts. We may contrast this experiment with the common one of accelerating the flow of water from a pierced can by electrifying it. In the last-mentioned case the loss of potential energy by the dissipation of the charge appears in an increase of heat produced by the impact of the falling drops. For, in the one case, electrostatic action causes the drops to fall less rapidly than they would if not electrified ; in the other, more rapidly.

116. But the voltaic arrangement furnishes by far the most powerful effects which can be obtained from the fundamental separation of electricities by contact. By interposing between two metals which have been electrified by contact, a compound liquid (or electrolyte), these metals are at once reduced to the same potential, a result which could not have been obtained by connecting them by any metallic conductor. By the passage of the electricity a portion of the electrolyte is decomposed, and the potential energy thus developed is equal to that possessed by the electricity while separated in the metals. Bring the metals into contact again, and the same series of operations may be repeated. This state of things is directly obtained if we close the circuit by connecting the metals by a wire, and then we have constant separation of electricities at the point of contact of different metals, and constant recombination, attended with decomposition, through the electrolyte.

117. This is an exceedingly imperfect view of the action of the galvanic battery, but it gives a general idea of the fundamental processes, and must suffice for the present at least, since the consideration of such complex phenomena as polarisation of the electrodes, etc., would lead us into details far too recondite for an elementary treatise. One or two very singular results of Joule's early investigations may be mentioned. It was shown by Faraday, that if the current from a battery passes through any number of cells, filled with any different electrolytes, the quantities of the various components set at liberty in a given time in each of the cells are proportional to the chemical equivalents of these components ; and that the quantity of zinc dissolved in each cell of the battery is determined by the same law. Besides the electrolytic action, there is of course a development of heat in the circuit. Hence, if the energy of chemical affinity consumed in the battery be less than that restored in the decomposing cell, we should have a production from nothing of energy in the forms of heat and chemical affinity. It appears from Thomson's calculations<sup>1</sup> that the electromotive force required for the decomposition of water is 1·318 times that furnished by a single cell of Daniell's battery.

He says, 'Hence at least two cells of Daniell's battery are required for the electrolysis of water ; but fourteen cells of Daniell's battery connected in one circuit with ten electrolytic vessels of water with platinum electrodes would be sufficient to effect gaseous decomposition in each vessel.'

118. In Joule's paper of 1843, on the heat of electrolysis, he showed that heat is generated in the circuit in *different* quantities by the electrical evolution of *equal* quantities of hydrogen at equal surfaces of *different* metals, thereby removing the difficulty arising from the fact, that in different batteries all with the same more oxidisable metal, the

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<sup>1</sup> On the Mechanical Theory of Electrolysis.—*Phil. Mag.* 1851.

electromotive force is found to vary with the other metal. Thomson,<sup>1</sup> by applying the principle of energy to some experimental results of Faraday, showed theoretically and experimentally that a feeble continued current passing out of an electrolytic cell by a zinc electrode, must generate exactly as much more heat at the zinc surface than the same amount of current would develop in passing out of an electrolytic cell by a platinum electrode, as a zinc-platinum pair working against great external resistance would develop in the resistance wire by the same amount of current. Thus, let a circuit be formed of three cells, each of water acidulated with sulphuric acid; with plates of zinc and platinum immersed in No. 1, zinc and tin in No. 2, and zinc and zinc in No. 3; the platinum of No. 1 being connected with the zinc of No. 2, the tin of No. 2 with one of the zincs of No. 3, and the other zinc of No. 3 with the zinc of No. 1. There will be precisely the same chemical action in each of the three cells; yet No. 2 will give only about half the electromotive force that No. 1 does; and No. 3 will give precisely none. That a tin-zinc element should give only about half the electromotive force of a platinum-zinc element, with precisely the same chemical action, and precisely the same mode and quantity of hydrogen evolved, had been felt as an objection to the electro-chemical theory, and prominently put forward as such by Poggendorff. The investigations of Joule and Thomson, just referred to, completely explain the difficulty, by proving that where the current leaves the liquid by the zinc plate in No. 3 cell of the circuit we have imagined, it experiences a reverse electromotive force exactly equal to the whole electromotive force of No. 1 cell; and where it leaves the liquid of No. 2 cell by the tin plate, it there experiences a reverse electromotive force equal to the excess of the direct electromotive force of No. 1 above that of No. 2; and that these reverse

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<sup>1</sup> *British Association Report*, 1852.

electromotive forces are the reactions of work done in generating heat at the zinc and tin electrodes over and above that (if any, whether positive or negative) at the platinum electrode of No. 1. It is to be remarked, farther, that the *whole heat* of the chemical action in No. 3 is developed in the cell itself, and that the excess of this above that developed in No. 1 is exactly equal to the thermal value of the work done externally by No. 1. The three papers just mentioned contain an immense amount of valuable matter which cannot possibly be given in such a work as this. ✓

119. The conservation of energy would hold in the case of the mutual actions of permanent magnets if their magnetisation were perfectly 'rigid,' because such magnetic attractions and repulsions can be completely accounted for by a distribution of an imaginary magnetic matter, each unit of which attracts or repels another with a force whose law is the same as that of gravitation; and which therefore satisfies the criterion (a) (§ 96) required by Helmholtz's investigation. But the perpetual-motionists have not yet given up attempts to construct self-driving engines by means of permanent magnets.

120. The force exerted by a voltaic current upon a magnet at rest is precisely the same as that exerted by a uniformly and normally magnetised open shell bounded by the circuit, and of strength proportional to that of the current, and is therefore also subject to the law of conservation. But if the magnet be allowed to oscillate under the influence of the current, it comes sooner to rest than it would do under the influence of the equivalent magnetic shell. In fact, if the experiment were made *in vacuo*, the needle would ultimately come to rest in the former case, but would maintain its oscillations undiminished for ever in the latter. In the former it evidently loses energy, in the latter it does not. [The hypothetical magnetic shell is supposed to be a non-conductor, and to be unaffected by magnetic

induction.] Now, with the principle of conservation to guide us, let us inquire what is the difference between the two cases. Experiment shows that the motion in the former case differs from that in the latter very much as if the magnet were moving in a resisting medium—the resistance being (*ceteris paribus*) dependent on the rate of motion at each instant. This alteration of the mutual action of current and magnet of course implies an alteration of the strength of the current, or what comes to the same thing, the superposition upon it of another current which depends solely upon the motion of the magnet, and is therefore independent of the strength of the original current in the circuit. More heat is, on the whole, generated in the circuit than that due to the loss of energy by chemical combination in the battery:—and this is exactly equivalent to the corresponding loss of energy by the magnet. In the *Appendix* (D) below will be found an extract from Helmholtz's pregnant pamphlet, which gives a very clear view of the relation of electro-magnetism and magneto-electricity deducible from the conservation of energy.

121. Now we might suppress the battery in the closed circuit, and the conservation of energy immediately suggests the question, Does the presence of this conducting body alter the amount of work necessary to produce a given motion of the magnet? Long ago, Arago observed that, if a copper plate be placed under a vibrating magnetic needle, the oscillations are very rapidly diminished, and the needle comes to rest much sooner than when left to itself. This *Damper*, as it is called, is still employed in galvanometers of faulty construction, where the great moment of inertia of the needles, and the small resistance opposed to their motion by the air, render their oscillations long-continued, and their observation tedious, and for many rapidly-changing phenomena their use *nil*. [There are, of course, galvanometers specially constructed to measure the 'time-integral' of the electro-magnetic force produced by the discharge of a con-

denser, etc. But these require no damper.] Subsequently, Arago showed that if the disc be made to rotate, it carries the needle with it. Faraday cleared up the whole subject in 1831, by his fine discovery of the induction of electric currents in the relative motion of a magnet and a conductor. The damper acts by the reaction (upon the needle) of the currents produced by the relative motion :—which Lenz showed to be such as in all cases to *resist* that motion ; and it is their energy, and, afterwards, that of the heat into which (by resistance to conduction) they are finally transformed, which forms the equivalent to the loss of energy by the vibrating needle.

122. We now see the complete explanation of the phenomena of mutual action of currents and magnets which we have already mentioned ; and whose full agreement with the theory of energy was experimentally shown by Joule in 1843. The magneto-electric machine, which depends entirely upon this principle, is employed on a large scale in many important applications ; for instance, it is employed in producing chemical decomposition, as in electroplating ; physiological effects, as in the ordinary medico-electric machines ; and light, as in the successful trials at the South Foreland Lighthouse, where an electric spark, much more luminous than the ordinary oil-lamp, was maintained by the work expended by a small steam-engine in turning before a series of electro-magnetic coils a wheel, to whose circumference a great number of powerful steel magnets was attached. It is also applied, on certain telegraphic lines, to the production of electric currents for the purpose of signalling.

123. It is only with the *relative* motion of the magnet and conductor that we are concerned, and therefore, although we have hitherto supposed the magnet to move in presence of the conductor, precisely similar effects will be produced if the conductor move in presence of the magnet. Thus, when we consider that the earth acts as an immense magnet

on all bodies near its surface, it is obvious that in general all motions of electric conductors are resisted by the earth's action upon the currents developed in them by their motion. Faraday suggested the application of this principle to the construction of a magneto-electric machine in which the earth takes the place of the usual permanent magnets. The apparatus consists simply of a copper disc made to rotate about an axis, and the electricity is collected by two wires, one of which touches the rim of the disc, while the other is connected with the axis. More work is required to turn this disc than would be required to turn with the same speed an equal disc of non-conducting matter, and this excess of work is entirely transformed into electric currents. If the axis of the disc be in the direction of the dipping-needle, the greatest possible amount of current-electricity is generated. If, instead of a conducting disc, a circular coil of wire be employed, rotating about a diameter, no current will be produced when the axis is in the line of dip. This result has been used by Thomson to ascertain the dip, and furnishes in fact a method which may probably be made very much more sensitive and accurate than that afforded by the instrument in common use: being entirely unaffected by friction, which is a most serious impediment to the working of the dipping-needle. But it is interesting to notice, as an immediate deduction from what has just been said, that the heat developed in all moving machinery is partly due to true friction, partly to the viscosity of air, and partly to the earth's magnetism. Thus, for instance, a gyroscope will spin longer if its axis be placed in the line of dip than in any other position, supposing all other circumstances the same.

124. There can be little doubt of the fact that magnetism consists in something of the nature of electric currents surrounding each separate molecule of the magnetic, or magnetised, body; especially since Ampère, by his construction of solenoids (or helical arrangements of conducting wires), produced, without iron or other magnetic metal, all



the phenomena of magnetic attractions, etc. Whether these currents exist naturally in all bodies, and are merely reduced by magnetising force to parallelism, or whether they are *created* by the magnetising force, matters little to the conservation of energy, so long as it is possible to show that in magnetising any body, and therefore endowing it with a certain amount of potential energy as regards other magnetic or magnetisable bodies and electric currents, a certain equivalent of energy is spent. Now this expenditure is always incurred, but quantitative determinations are wanting as to how much is spent in magnetising, how much in heat, sound, etc., which always accompany the magnetisation of iron. A very good instance of the conservation of energy is supplied by the fact, that even the softest iron takes *time* to acquire the full amount of magnetism due to any action of currents or other magnets; and that when the magnetising force is removed, it does not instantly lose its magnetism. If, therefore, a piece of soft iron be allowed slowly to approach a magnet, and be then rapidly withdrawn from it, the mutual attraction during the second part of the operation is greater at each stage than during the first, and therefore work must (on the whole) be spent in the process. The iron is restored to its former position, and in a little time its magnetism is lost. The work spent during the operation (neglecting the induced currents due to the relative motion, which are probably the same in iron as they would be in an equal mass of any non-magnetic substance of the same conductivity, and which tend to the same ultimate form) is entirely transformed into heat. If a similar experiment be made with a piece of unmagnetised steel, we have in the energy of the magnetism which it permanently receives the equivalent of the work spent.

125. That magnetism, whether in a magnetic or a diamagnetic body, depends upon motion, was shown by Thomson<sup>1</sup>

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<sup>1</sup> *Proceedings of the Royal Society*, 1856.

to follow as a necessary consequence of Faraday's beautiful discovery of the rotation of the plane of polarisation of a polarised ray of light produced by media under the influence of a powerful magnet. The general correctness of Ampère's hypothesis regarding the nature of magnetism may be considered as decisively established by this dynamical theory. Faraday had observed the effect in diamagnetic bodies only : but it was afterwards discovered, by Verdet, that the effect of a paramagnetic body is to produce rotation of the plane of polarisation in the opposite direction to that in a diamagnetic under the same conditions. It seems most probable, notwithstanding this discovery of Verdet's, that the rotations constituting magnetisation in a diamagnetic body, are in the same directions, but of less amount, than in the surrounding medium ; although the opposite has been held by many naturalists.

126. The commonly received opinion, that a diamagnetic body in a field of magnetic force takes the *opposite* polarity to that produced in a paramagnetic body similarly circumstanced, is thus attacked by Thomson by an application of the principle of energy. Since all paramagnetic bodies require time for the full development of their magnetism, and do not instantly lose it when the magnetising force is removed, we may of course suppose the same to be true for diamagnetic bodies ; and it is easy to see that in such a case a homogeneous non-crystalline diamagnetic sphere rotating in a field of magnetic force would, if it always tended to take the opposite distribution of magnetism to that acquired by iron under the same circumstances, be acted upon by a couple constantly tending to turn it in the same direction round its centre, and would therefore be a source of the perpetual motion.

127. Among the various applications of the Science of Energy, the proof of the mutual dependence of the different kinds of electromagnetic phenomena is interesting, as expressing in a distinct form the ideas which were gradually

developed by Ørsted and Ampère, and which constitute the scientific connection of Faraday's splendid chain of discoveries.

Helmholtz, in his tract on the *Conservation of Energy*, and W. Thomson, in his *Mechanical Theory of Electrolysis*,<sup>1</sup> working independently of each other, arrived at a proof on strictly mechanical principles, that if the phenomena discovered by Ørsted and Ampère be assumed, that is, if a wire carrying an electric current is impelled across the lines of magnetic force according to the observed laws, then the phenomenon discovered by Faraday necessarily follows, namely, a conductor moved across the lines of magnetic force experiences an electromotive force whose intensity can be completely determined by the application of the equation of energy.

In this way Thomson showed that the unit of electromotive force already adopted by W. Weber, independently of the principle of conservation of energy, is the only unit consistent with that principle.

128. Thomson<sup>2</sup> has also remarked that the energy of an electric current is kinetic energy, that is, it depends on the motion of matter. The matter in motion is not however simply in the conducting wire ; for the energy of the current depends on the form of the wire and the media in its neighbourhood, as well as on the length and thickness of the wire. He looks for this motion not merely in the wire itself, but also in the surrounding space, wherever the electromagnetic action extends, and he has given reasons for supposing that the motion is of the nature of rotation round the lines of magnetic force as axes.

Thomson, therefore, regards the medium which surrounds magnets and conductors as the seat of rotatory motions of great energy, which by their centrifugal force cause the

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<sup>1</sup> *Trans. British Ass.*, 1848 ; *Phil. Mag.* Dec. 1851.

<sup>2</sup> Nichol's *Cyclopædia*, Art. 'Magnetism.'

magnetic attractions. He has also shown that to account for the transmission of light and heat from the sun, we must admit that the interplanetary medium has a density by no means inappreciable.

129. This method of looking for the origin of electrical effects in the surrounding medium, as well as in the visible apparatus, is that which under the name of the method of Lines of Force is used so much by Faraday in his researches. Clerk-Maxwell<sup>1</sup> has expressed this method in mathematical language, and, by means of particular hypotheses<sup>2</sup> as to the molecular vortices, has shown how the various phenomena may be connected with one another. He seems, however,<sup>3</sup> to have since discarded these hypotheses, and to rely only on the principle of energy applied to investigate the properties of the medium which he supposes to be the cause of electromagnetic effect.

130. He assumes that there is a medium capable of transmitting light and heat, and therefore capable of storing up two kinds of energy, that of motion and that of elastic resilience, both which are exemplified in the case of luminous waves. The medium, if capable of these motions and stresses, may also be capable of others, and these may produce visible phenomena. Thomson has shown that the action of magnetism on polarised light indicates a state of motion wherever magnetic lines exist. Now, every current is surrounded by such lines, whose intensity depends on that of the current. There will, therefore, be a certain inertia to be overcome in starting the current, and a certain persistence in the current when started, just as in any piece

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<sup>1</sup> On Faraday's Lines of Force, *Camb. Phil. Trans.* 1857. [For this, and a great deal more than can be even indicated in our narrow limits, see Clerk-Maxwell's splendid work on *Electricity and Magnetism*, which was published in 1872.]

<sup>2</sup> On Physical Lines of Force, *Phil. Mag.* 1861-2.

<sup>3</sup> Dynamical Theory of the Electromagnetic Field, *Phil. Trans.* 1865. *Electricity and Magnetism*, 1872.

of wheelwork, the inertia of every wheel adds apparent inertia to the motions of the driving-wheel. From this Clerk-Maxwell has deduced, by Lagrange's dynamical equation,<sup>1</sup> the known laws of the induction of currents, and of the attraction of currents.

131. The force by which the motion of the medium is transmitted from one part of the field to another is called the electromotive force. If we suppose that when the electromotive force acts on a dielectric, it produces a kind of polarisation, or, as he calls it, an electric displacement, depending on the nature of the medium, then energy of a different kind will exist in the medium, similar to that which exists in a strained elastic body, and measured by the half product of the electromotive force and the electric displacement. From these assumptions he has deduced all the known laws of electricity and magnetism, except Ohm's Law of Conduction, which remains a primary fact.

132. On this theory of the electromagnetic field, Clerk-Maxwell has founded an electromagnetic theory of light. He determines from the equations representing the known laws of electricity the rate of propagation of any kind of disturbance. The physical quantities involved in this calculation have been already determined by W. Weber, and the resulting velocity of propagation of electromagnetic disturbance differs less from the mean of the various estimates of the velocity of light than these do from each other. This result goes far to strengthen the theory that both light and electricity are phenomena of a medium, by showing that the medium which is assumed to explain the one set of phenomena is capable of explaining the other. By taking the more general case of a medium having different properties in different directions, the electromagnetic theory leads to the conclusion that only *two* velocities of propagation are possible, both corresponding to *transverse* disturbances, and

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<sup>1</sup> Thomson and Tait. *Nat. Phil.*, § 293.

that the disturbance *normal* to the wave, which forms so great a difficulty in the ordinary form of the undulatory theory, is incapable of being propagated. The experiments of Holtzmann on spheres of crystallized sulphur agree with this theory.

Another result of his theory is that the dielectric capacity of a substance is equal to the square of its index of refraction. The experiments of Holtzmann,<sup>1</sup> Schiller,<sup>2</sup> and Silow,<sup>3</sup> seem to show that this is true very exactly for gases, and approximately for solids and liquids. But Hopkinson<sup>4</sup> has shown that in glass there is no approach to agreement.

133. In the preceding chapter, Seebeck's discovery of the production of electric currents by unequal heating in any non-homogeneous conductor was merely mentioned; we must now consider, as a case of the conservation of energy, the transformation of heat into work which would be effected by applying such currents to drive an electromagnetic engine.

134. If the ends of an iron wire be attached by twisting or soldering to the extremities of the copper wire of a galvanometer, and one of these junctions be heated, the galvanometer indicates the passage of a current in the circuit in a direction from copper to iron through the heated junction. The first application of the theory of energy to this phenomenon is of course as follows:—Since heating the junction produces the energy of the current, part of the heat must be expended in this process; though it is of course entirely recovered as heat in the circuit, if the current be not employed to do external work. The existence of the current from copper to iron is thus associated with absorption of heat in the junction; agreeing with Peltier's remarkable discovery that if an electric current be passed through a circuit of iron and copper, originally at the same temperature throughout, it produces cold when passing from copper to iron, and heat when passing from iron to

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<sup>1</sup> Vienna *Sitzungsb.* 1870.

<sup>2</sup> *Pogg.* clii. 535.

<sup>3</sup> *Pogg.* clvi.

<sup>4</sup> *Froc. R.S.* 1877.

copper. If the two junctions be maintained each at a constant temperature, a constant current passes from the warmer to the colder junction through the iron wire; and by the principle of conservation of energy, the heat developed in the circuit (together with the equivalent of the external work done, if the current be employed to drive an electro-magnetic engine) must be equal to the excess of the heat absorbed at the warmer junction over that given out at the colder, precisely as in the case of a heat-engine. So far the process presents no difficulties. But it was discovered by Cumming<sup>1</sup> in 1823, that not only is the strength of the current *not* generally proportional to the difference of temperatures of the junctions, but that if the difference be sufficiently great the current may, in many cases, pass in the opposite direction. In the copper-iron circuit, if the temperature of one junction be at the neutral point (about 270° C., for the exact temperature varies with the specimens of the metals), the current passes through it from copper to iron, whether the other junction be colder or warmer. Thomson<sup>2</sup> applied the principle of energy to this case, and derived from it the conclusion that one of three things must happen, the most unexpected of which he found by experiment to be the actual one, viz., the startling result that *a current passing in an iron bar or wire from a hot to a cold part produces a cooling, but in copper a heating effect*. This very remarkable discovery, which, taken in connection with that of Peltier, gives the key to the whole subject of Thermo-electricity, has been recently made the subject of a valuable experimental investigation by Le Roux,<sup>3</sup> who has found the so-called 'specific heat of electricity' to be null in lead. Tait<sup>4</sup> has since shown that in general, for ordinary ranges of temperature this *electric convection* of heat

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<sup>1</sup> *Camb. Phil. Trans.*

<sup>2</sup> Bakerian Lecture—*Phil. Trans.* 1855—'On the Electrodynamical Properties of Metals.' Also *Proc. R. S. E.*, Dec. 1851.

<sup>3</sup> *Annales de Chimie*, 1867.

<sup>4</sup> *Proc. R. S. E.* 1868, 1871-2; *Trans. R. S. E.* 1873; Rede Lecture—*Nature*, 1873.

is proportional to the absolute temperature. This seems to be at least approximately the case for the great majority of ordinary metals through very wide ranges of temperature, almost in fact up to their melting points. But iron and nickel exhibit the curious phenomenon of *change of sign* of their Thomson effect. This takes place at least twice in each of these metals as their temperature is gradually raised. Thus we can construct an ordinary thermo-electric circuit of two metals in which there shall be no Peltier effect at all. [In this case the current is maintained wholly by the Thomson effect; which, if the second metal be properly chosen, may be confined entirely to the iron or nickel.] This may also be effected, of course, by making a circuit of any *three* metals, and raising the junction of each two to their neutral point.

135. The theory of such phenomena (and of others far more complex, involving, for instance, crystalline arrangement), in complete accordance with the conservation of energy, has been given by Thomson,<sup>1</sup> but it would be inconsistent with the character of this work to enter into any details on such a subject. A similar remark must be made regarding his application of the principle to the subject of Thermo-magnetism, or the relation of the magnetisability of various substances to their temperature; one or two of his results may, however, be mentioned. Thus, iron, at a moderate or low red heat must experience a heating effect when allowed to approach a magnet, and a cooling effect when slowly drawn away from it; while in cobalt, at ordinary temperatures, exactly the opposite effects must be produced. Similar effects must in general be produced when a doubly-refracting crystal is turned in the neighbourhood of a magnet.

136. Magnus showed that sudden contact between the ends of a wire, at different temperatures, produces a temporary current, which, in copper, is from the cold to the warm end across the junction, but in the opposite direction in platinum.

137. This meagre sketch of the general application of the

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<sup>1</sup> *Trans. Royal Soc. Edin.* 1854.



principle to the chief phenomena of experimental physics (an application which is every day indicating how to co-ordinate some newly discovered fact, and even occasionally to predict the result of a perfectly novel experimental combination) will be closed by the brief consideration of an instance or two which must be familiar to most readers. Thus, in the case of the galvanic battery employed to decompose water, we have the potential energy of chemical affinity in the battery to begin with. This is probably first transformed into electric motion; in fact, according to Joule, heat of combination, like that of friction, is in all likelihood due to resistance to conduction. Part of it, then, becomes heat, which is developed simultaneously in all parts of the circuit, and the rest is expended in producing potential energy in the form of the explosive mixture of oxygen and hydrogen. Thus, if the poles be connected, first directly by a wire, and secondly with the decomposing cell interposed in the circuit, and the action be allowed to go on in each case till the same given quantity of zinc has been dissolved in the battery; the heat developed in the whole circuit will be greater in the first case than in the second, by a quantity which can at any future time be obtained by exploding the mixed gases. The sound produced (with the mechanical energy of the fragments of the eudiometer, if it should burst) ultimately becomes heat, and the flash and heat of the explosion are already in that form. Should the battery be made to drive an electro-magnetic engine which is employed in raising weights, in this case also less heat will be generated in the whole circuit than is equivalent to the consumption of zinc in the cells; but in the form of the raised weights this energy is stored up, to take its final transformation into heat at any distance from the battery, and after any interval of time however long. This is one of the finest of Joule's discoveries, that chemical combination (*i.e.* combustion) may be made to take place without generating at once its full equivalent of heat.

138. Ruhmkorff's induction-coil is another beautiful in-

stance of varied transformations of energy. While it is in action we have light, sound, heat, electricity, and motion of gross matter, all simultaneously produced, and representing separate portions of the potential energy which is disappearing in the battery. Ultimately, in this case also, the whole energy which thus disappears takes the final form of heat.

139. A most important question arising naturally from the consideration of the laws of energy is that of the economic production of any species of work. We have seen that in *all* actual processes of transformation, energy must be dissipated, and therefore it becomes necessary to inquire what modes of transformation are least imperfect. In the preceding chapter we gave Thomson's formula for the proportion of usefully applied heat in the steam or air engine. The fraction of the whole energy which is there wasted is formed by dividing the lower absolute temperature employed by the higher. The reason of the superiority of the air-engine over the steam-engine, as depending on this, has been already pointed out. Joule had proved in 1846<sup>1</sup> that, when a battery drives an electro-magnetic engine, the fraction of the chemical energy which is wasted in the form of heat is found by dividing the strength of the current when the machine is at work by the strength when it is at rest (which is of course the greater of the two). And he observes that this follows from the fact which he had previously proved, that the heat developed is proportional to the square of the strength of the current, combined with Faraday's discovery, that the strength of the current is proportional to the amount of zinc dissolved in a given time.<sup>2</sup>

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<sup>1</sup> Scoresby and Joule on the *Mechanical Powers of Electro-magnetism, Steam, and Horses*.—*Phil. Mag.*

<sup>2</sup> In symbols,  $Z$  being the amount of potential energy lost by zinc,  $I$  the intensity of current,  $R$  the resistance :—

$$Z_1 = RI_1^2, \text{ when no work is done,}$$

$$Z_2 = RI_2^2 + W.$$

These express Joule's Law. But by Faraday's Law  $Z_1 : Z_2 :: I_1 : I_2$ .

Hence fraction of energy usefully expended  $= \frac{W}{Z_2} = \frac{I_1 - I_2}{I_1}$ .

140. Rankine<sup>1</sup> has shown, from general principles of energy, that a similar formula must hold in every case of transformation ; so that we have the means of determining the useful effect of any combination as soon as certain easily-attained experimental data have been found.

141. The superiority of the air-engine to the steam-engine depends on the fact that we can, with safety, use far greater ranges of temperature in the former than in the latter. If a frictionless electro-magnetic engine could be constructed in which the driving current would be very greatly reduced by induction, and if the fuel for the battery (zinc and sulphuric acid) could be produced at anything like the cost of a mechanical equivalent of coal and oxygen, there can be no doubt that the heat-engines would soon be superseded by the electro-magnetic. But this is, as yet, perfectly hopeless ; for, although the faster the electro-magnetic engine turns the smaller is the proportionate waste of energy as far as the battery is concerned, yet the waste by ordinary friction becomes enormously increased.

142. Very few remarks upon the physiological applications of the laws of energy need be made here, since the subject has been most ably discussed by Helmholtz, in a series of lectures at the Royal Institution, of which copious abstracts have been published in an accessible form.<sup>2</sup>

In the appendix to Joule's paper of 1843 already referred to, we find the following most suggestive sentence :—

‘ If an animal were engaged in turning a piece of machinery, or in ascending a mountain, I apprehend that, in proportion to the muscular effort put forth for the purpose, a *diminution* of the heat evolved in the system by a given chemical action would be experienced.’

Mayer's pamphlet of 1845 adds considerably to the development of the question. He speculates acutely on the merely

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<sup>1</sup> *General Law of the Transformation of Energy.*—*Phil. Mag.* 1853.  
*The Science of Energetics.*—*Edin. Phil. Jour.* 1855.

<sup>2</sup> *Medical Times and Gazette*, April 1864.

*directive* agency of the so-called *Vital Force*, and gives some excellently chosen illustrations of his views. Recent researches in chemical synthesis have broken down many of the supports on which the old theory of vital force rested, and the mode of its action remains in consequence exceedingly obscure. But there can be little doubt that, as Joule suggested (in his paper of 1846 already quoted from), an animal more closely resembles an electro-magnetic, than a heat, engine. And it is wonderful that it is a far more economic engine than any which we are yet able to construct. The first idea of this seems to have been entertained by Rumford, for he expressly shows, in his paper quoted from in the preceding chapter, that the amount of work done by a horse is much greater than could be procured by employing its food as fuel in a steam-engine. Simple illustrations of the application of conservation of energy to animal processes are found in hibernating animals, which expend a great part of their substance during the winter in maintaining the animal heat: and in the greater supply or choicer quality of food required by convicts in penal servitude, than by others who are merely imprisoned.

143. Between animals on the one hand, and the majority of plants on the other, there is a fundamental difference in the application of the laws of energy. In the animal we have chemical combination attended with the production of heat, muscular energy, etc., as transformations of the potential energy of the food (in which, of course, the air inhaled is to be included). In plants, on the other hand, carbonic acid and water, the energy of whose constituents has been lost in animals, are again decomposed, and their potential energy stored up afresh, so that they are once more adapted for food or fuel. It is obvious that this process would be inconsistent with the conservation of energy unless the plant during its growth were supplied with energy from external sources sufficient to account for the energy apparently restored. This external supply is

given to plants in a radiant form from the sun. Their green leaves absorb readily, and almost completely, those portions of the light which fall on them which are capable of producing chemical changes. This is beautifully illustrated by the processes of photography. The green light which leaves scatter or allow to pass through them, produces scarcely any effect on the most sensitive photographic preparations; and one of the greatest imperfections of the beautiful art of Daguerre and Talbot, the unnatural blackness of the foliage in photographic landscapes, is due to this cause. So far as is yet known, this is a defect which cannot be wholly cured. Thus it appears that we may compare (roughly) an animal supplied with food to a galvanic battery, in which chemical affinity is exhausted in producing electric motion, heat, and mechanical work; while a plant resembles a cell containing an electrolyte, or a photographic plate, in either of which energy supplied from without in the form of electricity or light is transformed into a restoration of potential energy of chemical affinity. Of course the analogies are by no means complete, but they are sufficient to give the reader a rough idea of the essential difference between the two forms of organic life. For, though by far the greater portion of the energy of the food supplied to an animal is dissipated directly or indirectly as heat, a portion is stored up as potential energy in its flesh, which in turn is employed as the food of man or other animals, or even of the animal itself. And a corresponding deviation, but in the opposite direction, takes place in plants, where radiant kinetic energy is to a certain extent devoted to the formation of complex products, which, though necessary to animal life, cannot be produced in the animal system.

**144.** The energy at present directly available to man for the production of mechanical work is almost entirely potential, and consists mainly of—

1. Fuel;
2. Food of Animals;

3. Ordinary water-power ;

4. Tidal water-power ;

These will presently be considered more closely ; but we have also energy in a kinetic form, as—

5. Winds and Ocean-currents ;

6. Hot Springs and Volcanoes ; etc. etc.

**145.** The immediate sources of these supplies are four :—

I. Primordial Potential Energy of Chemical Affinity, which probably still exists in native metals, possibly in native sulphur, etc., but whose amount, at all events near the *surface* of the globe, is now very small.

II. Solar Radiation.

III. The energy of the earth's rotation about its axis.

IV. The internal heat of the earth.

**146.** Thus, as regards (I.), our supplies of fuel for heat-engines are, as was long ago remarked by Herschel and Stephenson, mainly due to solar radiation. Our coal is merely the result of transformation in vegetables, of solar energy into potential energy of chemical affinity. So, on a small scale, are diamond, amber, and other combustible products of primeval vegetation. Though (II.) thus accounts for the greater part of our store, (I.) must also be admitted, though to a very subordinate place.

As to (2.), the food of all animals is vegetable or animal, and therefore ultimately vegetable. This energy then depends almost entirely on (II.) This also was stated long ago by Herschel.

Ordinary water-power (3.) is the result of evaporation, the diffusion and convection of vapour, and its subsequent condensation at a higher level. It also is mainly due to (II.)

Tidal water-power (4.), although not yet much used, is capable, if properly applied, of giving valuable supplies of energy. As the water is lifted by the attraction of the sun and moon, it may be secured by proper contrivances at its higher level, and there becomes an available supply of

energy when the tide has fallen again. Any such supply is, however, abstracted from the energy of the earth's rotation (III.)

Winds and ocean currents (5.), both employed in navigation, and the former in driving machinery, are, like (3.), direct transformations of solar radiation (II.)

So far as this brief and imperfect summary (which it would be easy to extend indefinitely) goes, there remain to be considered only (6.) Hot Springs and Volcanoes, due to (IV.), but of which no application to useful mechanical purposes has yet been attempted.

147. We must next very briefly consider the origin of these causes, with the exception of (I.), which is of course primary; though possibly related to gravitation. Helmholtz, Mayer, and Thomson come to our assistance, and suggest as the initial form of the energy of the universe the potential energy of gravitation of matter irregularly diffused through infinite space. By simple calculations it is easy to see that, if the matter in the solar system had been originally spread through a sphere enclosing the orbit of Neptune, the falling together of its parts into separate agglomerations, such as the sun and planets, would far more than account for all the energy they now possess, in the forms of heat and orbital and axial revolutions. It is not necessary to enter here into details as to the amount of each of these forms of energy in the members of the solar system. The reader will find them given with more or less detail in the writings of the three authors just named. Thomson's numerical results, with reference to the '*Age of the Sun's Heat*,'<sup>1</sup> are amongst the most recent, and are probably the most accurate of any that have been given on this vast subject. It is sufficient to observe that these calculations entirely forbid the supposition once entertained, that the sun's heat is due to chemical combination (or combustion). If the sun's

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<sup>1</sup> *Macmillan's Magazine*, 1862.

whole mass were composed (in the most effective proportions) of the known bodies which would give the greatest heat of combination, the entire heat that could be developed by their union would but supply the sun's present loss by radiation for 5000 years. But geological facts show that for hundreds of thousands of years the sun has been radiating at its present, if not at a much higher, rate. The potential energy of gravitation is the only known antecedent capable of accounting for the common facts of the case. And the sun still retains so much potential energy among its parts, that the mere contraction by cooling must be sufficient (on account of the diminution of potential energy) to maintain the present rate of radiation for ages to come. In other words, the capacity of the sun's mass for heat, on account of the enormous pressure to which it is exposed, is very great. Thus (on the least, and most, favourable assumptions), from seven to seven thousand years must elapse, at the present rate of expenditure, before the temperature of the whole is lowered by one degree Centigrade.

148. As regards the transformation of energy, this presumed origin of the sun's radiation is most instructive, and we have only to notice the as yet unexplained relations which have been observed to exist between solar spots on the one hand, and two such distinct phenomena as terrestrial magnetism and planetary configurations on the other, to show that the grand subject has as yet been barely *sketched*; and that every step towards filling in the details will be of importance as well as novelty in science.

149. As regards dissipation of energy, all the members of the solar and stellar systems are of course in the position of hot bodies cooling. The smaller bodies would of course be less heated by the agglomeration of their constituents than the larger; and, even if they had been equally heated, would cool faster. The original fluidity of all the larger masses is attested by their nearly spherical forms, rendered more or less oblate by their axial rotations. Dissipation by radia-



tion takes place very freely until the surface cools sufficiently to solidify to some little depth; and is then, on account of the low conductivity of rock masses, reduced to a very slow rate. Though a great portion of the interior of the earth must be still at a high temperature, the surface temperature is not perceptibly increased by conduction through the crust. The sun, however, has been calculated to give out energy so profusely, that the radiation from one square foot of its surface amounts to 7000 horse-power. This estimate is probably too low, as no account is taken of possible absorption by the matter which fills all space between the earth and sun.

150. But while the heat of the sun and planets is thus being lost by dissipation, the energy of their axial and orbital motions is, on account of resistance, being gradually converted into heat. This process is so slow that its effects have as yet been observed only on one of the smaller comets, but it is so persistent that all the planets will in time fall in to the sun, whose store of energy will thus be for a short time recruited. One noticeable point in Mayer's *Celestial Dynamics* is the effect of tidal friction in dissipating the energy of a planet's axial rotation, an effect which Adams and Delaunay have recently proved to exist in the case of the earth.<sup>1</sup> [J. Thomson had taught this eight years before Mayer. It appears, however, that the first suggestion of such an effect is due to Kant.<sup>2</sup>] The general tendency of tides on the surface of a planet is to retard its rotation till at last it turns always the same face to the tide-producing body: and it is probable, as seems to have been first noticed by Helmholtz,<sup>3</sup> that the remarkable fact that satellites generally turn the same face to their

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<sup>1</sup> Thomson and Tait's *Nat. Phil.*, § 830.

<sup>2</sup> *Nature*, vii. p. 241.

<sup>3</sup> *Wechselwirkung der Naturkräfte*—Königsberg, 1854. Translated in *Phil. Mag.* 1856, i.

primary is to be accounted for by tides produced by the primary in the satellite while it was yet in a molten state.

151. Numerous and beautiful though they have been, especially in the writings of Mayer, the applications of the laws of energy to the solar system are yet merely in their infancy ; and, till they have been carried into further detail, we can expect to make but little from their application to stellar or nebulous systems, of which our knowledge is so small in comparison.

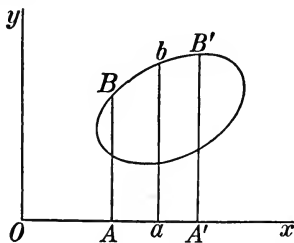
152. In this short account of the discovery and development of the grand laws of nature, so far as they are yet understood, the illustrations have been confined to the simplest cases ; and the reader must not imagine that he has been introduced to more than a small fraction of the known facts which have been directly shown to agree with them. It is as if, in treating of the theory of gravitation, his information had been restricted to the proof that Kepler's laws of the planetary motions follow from it, and that it enables naturalists to compare the masses of the earth and sun ; without his being made aware that lunar and planetary perturbations, precession and nutation, and far more recondite facts, are also perfectly explained by it. For the same reason our account contains but a small number of names, few philosophers being mentioned save those who have made really novel and considerable additions to our knowledge of the subject of energy ; though there are many others, both experimenters and mathematicians, whose work is of great importance, whether as regards the minuter details, or the more practical applications of the whole theory.

## CHAPTER III.

### SKETCH OF THE FUNDAMENTAL PRINCIPLES OF THERMODYNAMICS.

**153.** THE graphic method introduced by Watt, and still extensively employed, especially in the testing of steam engines, supplies a valuable geometrical representation of the changes of volume and pressure of the working substance, and of the work done during these changes. It was employed, as we have seen (§ 29), by Clapeyron; and it has since been ably applied by Rankine, to whose paper<sup>1</sup> the reader is referred for detailed information. We introduce it here, as it is easily intelligible even to those who cannot follow the analytical investigations which we must give further on.

**154.** Let the successive volumes of the working substance (which may be gas, vapour, or liquid, or even liquid and vapour together, provided it have at every instant the same pressure throughout) be represented by lengths ( $OA$ ) measured along the line  $Ox$ , and the corresponding pressures by lines ( $AB$ ) parallel to  $Oy$ . The extremities ( $B$ ) of these lines will trace the curve called *Watt's Diagram of Energy*: and the fundamental property is that any area such as  $AB B' A'$ ,



<sup>1</sup> *Phil. Trans.* 1854.

bounded by the curve, two ordinates, and the axis  $Ox$ , represents the external work done by the substance during its expansion from volume  $OA$  to volume  $OA'$ . Hence, as we may draw any curve whatever from  $B$  to  $B'$ , and so apply heat to the working substance that this curve shall represent the relation of pressure to volume during the expansion, it is evident that the work done cannot generally be expressed in terms of the initial and final conditions of the substance.

155. For the present it is sufficient to suppose that the working substance is confined in a cylinder with a movable piston. Suppose  $S$  to be the area of the piston, and  $ab$  (in the figure) the mean value of the pressure per square inch during the expansion, then  $S.ab$  is the mean value of the whole pressure upon the piston. Also, if  $\sigma$  represent the space through which the piston moves while the volume increases from  $OA$  to  $OA'$ , we have

$$S.\sigma = AA'.$$

Multiplying both by  $ab$ , we have

$$S.ab.\sigma = ab.AA'.$$

But the first of these quantities represents the whole external work done (being the product of the mean pressure on the piston into the space through which the piston has moved), and the second represents the area  $ABB'A'$ .

156. During a complete cycle of operations, at the end of which the working substance is restored exactly to its initial state, the point  $B$  must describe a *closed* curve; and, by what has just been proved, the area of this curve represents the excess of the work done (during expansion) upon external bodies, over that done (during contraction) from without upon the contents of the cylinder. And, since the working substance has been restored to its initial condition, the first law of thermodynamics (§ 52) shows us that *this area represents, in dynamical measure, the amount of heat which has been put out of existence during a complete cycle of*

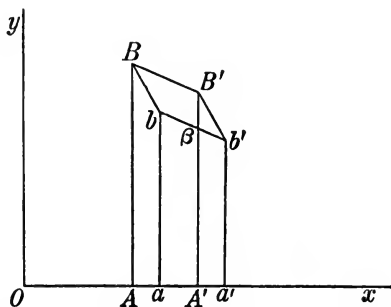
operations. To express this quantity of heat in the ordinary way, we must divide it by Joule's Equivalent. If the body be made to contract at higher temperatures and allowed to expand at lower, *the same area will represent the amount of heat created by the excess of work done on the body (during compression) over that done by the body (during expansion).*

157. The nature of the curve  $BB'$  depends, as we have seen, on the mode in which heat is applied to the working substance: and it is unnecessary to study it in its most general form. We may therefore restrict ourselves to the consideration of the two cases most commonly approximated to in practice, and most easily treated in theory, viz., when either, 1° the working substance is kept at a constant temperature during change of volume, or 2° when it is prevented from gaining or losing heat by conduction during its changes. These cases have been described above (§ 23); the first being the case when the cylinder is set on either of the bodies  $A$  or  $B$ , the second when it is set on the non-conducting stand  $C$ . Experiment shows that, when the substance is prevented from gaining or losing heat by conduction, its pressure in general diminishes faster with increasing volume than when the temperature is maintained constant. But, in either case, the pressure may be reduced below any assigned amount by a sufficient increase of volume. For *first*:—increase of pressure with increase of volume would necessarily involve instability—and such a state could not exist for any finite time; and, *secondly*, asymptotic diminution of pressure to a constant value, if the volume be allowed to increase, would furnish us with a source of the Perpetual Motion.

158. The propositions of § 156 are direct consequences of the first law, or the equivalence of heat and mechanical effect. In order to examine the second law, which will enable us to find *how much* of the heat communicated to the working substance can be transformed into work, we must introduce the principle of *reversible* cycles.

We may observe, generally, that any cycle is reversible if the working substance be throughout in contact either with non-conductors, or with bodies at its own temperature. The variety of such cycles is, of course, infinite. But for our present purpose it is sufficient to consider infinitely small changes of volume; since, if the cycle be reversible for all such, it will necessarily be reversible for finite changes, every finite cycle being capable of being broken up into an infinite number of infinitesimal ones.

159. Let us suppose that the working substance is allowed to expand while kept at a constant temperature,  $t$ , the requisite quantity of heat being supplied to it, and that while its volume thus increases from  $OA$  to  $OA'$ , its pressure sinks (§ 157) from  $AB$  to  $A'B'$ . Let it farther expand to volume  $Oa'$  and pressure  $a'b'$  while confined in the non-conducting vessel, so that its temperature undergoes an infinitesimal change,  $\tau$ ; the line  $B'b'$  sinks more rapidly than  $BB'$  (§ 157). Let it next be compressed, at the tempera-



ture  $t - \tau$ , to such volume,  $Oa$ , and pressure,  $ab$ , that when, finally, it is compressed in the non-conducting vessel to its original volume  $OA$ , it will have regained its original pressure  $AB$ , and therefore also its original temperature  $t$ . The whole external work done is represented by the closed area  $BB'b'b$ , which obviously becomes more and more nearly a

parallelogram as the changes of volume and temperature are smaller.

160. Also since, during the whole process, the working substance is surrounded either by bodies at its own temperature or by non-conducting bodies, the process is essentially a reversible one (there having been no transference of heat between bodies of different temperatures), and therefore it gives (§§ 26, 53) the maximum amount of work for the heat employed.

Also, as the heat drawn from the source is obviously proportional to the infinitely small change of volume,  $AA'$ , produced during the first stage of the operation, it may be represented by  $M.AA'$ , where  $M$  is a quantity whose value is to be studied. Even when  $AA'$  is finite, this expression will represent the heat taken in if the *average* value of  $M$  be employed.

161. Thus, *for all substances*, the ratio of the area of the figure  $Bb'$  to  $M.AA'$  (the quantity of heat taken in in the first operation) is constant for the same initial and final temperatures, and this whether the changes be indefinitely small or finite. But if they be considered, as above (§ 158) suggested, to be infinitely small,  $Bb'$  is a parallelogram: and its area is proportional to  $\tau$ , the difference of the extreme temperatures, and the ratio above mentioned becomes the product of  $\tau$  by a function of either temperature. Hence we have, for all substances,—

$$\frac{\text{Area } Bb'}{M.AA'} = JC\tau,$$

where  $C$  is a function of  $t$  alone, and  $J$  is Joule's equivalent.

162. Now, if  $A'B'$  meet  $bb'$  in  $\beta$ , the area of the parallelogram  $Bb'$  is

$$B'\beta \times AA'.$$

Substituting this expression for the area of the parallelogram in the equation preceding, we have

$$\frac{B'\beta}{M} = JC\tau.$$

But  $B'\beta$  is the change of pressure, at constant volume, due to the infinitesimal increase,  $\tau$ , of the temperature, so that we have

$$B'\beta = \frac{dp}{dt} \tau.$$

Hence the second law of thermodynamics may be expressed in the form

$$\frac{\frac{dp}{dt}}{M} = JC.$$

where  $C$  is *Carnot's Function* (§ 26).

This extremely remarkable proposition is entirely due to Carnot, but its truth is to be considered as established by reasoning similar to that of § 53 above, as Carnot in his demonstration assumed the materiality of heat.

163. Before we can go any farther, we must know exactly what we mean by *temperature*, for it is obvious that, because the quantity  $C$  has a perfectly definite value for each temperature, different modes of defining temperature (and it must be remembered that the measure of temperature is to a great extent arbitrary) will give different forms of expression for  $C$ .

164. *Def.* Two bodies are said to have the same temperature, when neither parts with heat to the other if they be put in contact.

The *numerical* measure of temperature is usually made to depend upon the changes of volume of some substance kept at constant pressure; and the changes of this numerical measure are taken to be proportional to those changes of volume. No two thermometers, filled with different substances, and graduated on this principle, give entirely concordant results; but the permanent gases, as air and its constituents, hydrogen, marsh-gas, carbonic oxide, etc., deviate very slightly from one another.

165. As the absolute measurement of temperature, though a point of fundamental importance in Thermo-



dynamics, seems to be treated (by most of the few writers who allude to it) in a manner neither satisfactory nor even accurate, it may be useful to devote a few sections to an elementary exposition of the question.

166. In every thermometric scale at present in use, two phenomena which occur at fixed temperatures, as the melting of ice and the boiling of water at given pressure, are selected, and denoted by definite numbers, as  $0^\circ$  and  $100^\circ$  for the Centigrade,  $0^\circ$  and  $80^\circ$  for Reaumur's, and  $32^\circ$  and  $212^\circ$  for Fahrenheit's scale.

To compare any other temperature,  $t$ , with these, the apparent volume of a substance which is convenient for thermometric purposes is observed at the fixed temperatures  $T_0$ ,  $T_1$ , and the unknown temperature  $t$ , and found to be  $V_0$ ,  $V_1$  and  $v$ . Then the temperature  $t$ , as measured by this thermometer, is found by assuming that the expansion is proportional to the change of temperature, or

$$\frac{T_1 - t}{T_1 - T_0} = \frac{V_1 - v}{V_1 - V_0}.$$

The indications of a particular thermometer, graduated in this way, are perfectly definite, each degree indicating a particular temperature, but thermometers of different substances do not, in general, agree with one another in any part of their scale except the standard points, because the substances of which they are composed have generally different rates of expansion at different temperatures.

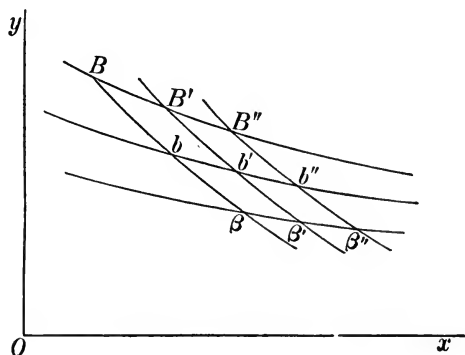
By correcting all thermometric scales so as to agree with that of some one standard thermometer, we might insure that the same temperature corresponds to the same degree; but, even in this case, such an equation as

$$t_1 - t_2 = t_3 - t_4$$

would give results depending upon the particular standard employed.

167. The true method of measuring temperature, founded on the dynamical theory of heat, is independent of the

substance employed; and, though requiring a more elaborate procedure, leads to results of a really definite kind. When the scale of some standard thermometer has once been accurately tested and corrected by this method, any common thermometer may be compared with it, and may be practically employed in the determination of absolute temperatures in the ordinary way.



168. Let the co-ordinates of  $B$  indicate the pressure and volume of unit of mass of the working substance at the commencement of the experiment; its temperature being  $T_1$ , say that of saturated steam at given pressure.

Let heat be communicated to the body, and let it expand at constant temperature till one unit of heat has entered.

Let its pressure and volume be then indicated by the co-ordinates of the point  $B'$ .

Similarly, let  $B''$ ,  $B'''$ , etc., indicate the state of the body when two, three, etc., units of heat have been communicated to it at temperature  $T_1$ .

From the points  $BB'B''$ , etc., draw curves  $Bb\beta$ ,  $B'b'\beta'$ , etc., indicating the relation between volume and pressure, when no heat is communicated to or taken from the substance. These curves are called *Adiabatic* lines.

Let  $\beta\beta'\beta''$  be a curve corresponding to a certain other fixed temperature  $T_0$ , say that of ice melting at given pressure, and let  $bb'b''$  correspond to some other temperature, which we may call  $t$ . It is required to determine the value of  $t$  in terms of  $T_1$ ,  $T_0$ , and the areas  $Bb'$ ,  $b\beta'$ , and  $B\beta'$ . Here  $B\beta'$  is the work done by a perfect engine, working between the temperatures  $T_1$  and  $T_0$ , for each unit of heat supplied. And thus, by § 26, we see that if the body be compressed from the state  $\beta'$  to the state  $\beta$ , at constant temperature  $T_0$ , the heat given out bears to one unit of heat the ratio of the heat given out to that taken in by any reversible engine working between the temperatures  $T_1$  and  $T_0$ . This is the thermodynamic problem.

169. Thomson's earliest method (§ 26) was to define equal differences of temperature, as those of the source and refrigerator in a reversible engine when the percentage of work produced from a given amount of heat is the same. But this definition had the inconvenience of giving a scale differing greatly from the mercurial, air, and other ordinary thermometers; the degrees defined by it corresponding to larger and larger intervals on the air thermometer as the temperature is higher. Besides, on such a scale, the temperature of a body totally deprived of heat is negative-infinite.

170. The observation of Joule (§§ 47 footnote, 64), as to the probable form of Carnot's function in terms of temperature by the air thermometer, was therefore afterwards made the foundation of the following definition of absolute temperature.

*Carnot's function is inversely proportional to the temperature from absolute zero.*

Thomson has put this in another, and apparently different, form—though, as will be seen in § 175, it is really the same. He says:—‘The temperatures of two bodies are proportional to the quantities of heat respectively taken in and given out in localities at one temperature and at the

other, respectively, by a material system subjected to a complete cycle of perfectly reversible thermo-dynamic operations, and not allowed to part with or take in heat at any other temperature: or, the absolute values of two temperatures are to one another in the proportion of the heat taken in to the heat rejected in a perfect thermo-dynamic engine, working with a source and refrigerator at the higher and lower of the temperatures respectively.”<sup>1</sup>

Thus defined, the *absolute* scale of temperature is of immense importance. It is independent of the substance on which we operate; our theoretical investigations become marvellously simplified; and the new scale has been experimentally shown by Joule and Thomson to differ but slightly from that of the ordinary air thermometer.

171. The elements referred to in § 170 being exhibited in the diagram of § 168, the definition of § 170 gives

$$\frac{T_1}{1} = \frac{t}{1 - \frac{B\beta'}{J}} = \frac{T_0}{1 - \frac{B\beta'}{J}} \quad \text{Hence } T_1 - T_0 = T_0 \frac{\frac{B\beta'}{J}}{1 - \frac{B\beta'}{J}}.$$

But if  $T_1$  be the temperature of saturated steam under pressure equal to that of 760<sup>mm</sup> of mercury at the freezing point, at the sea level in latitude 45°, and  $T_0$  be that of melting ice, we have by definition  $T_1 - T_0 = 100$ .

Hence

$$T_0 = 100 \frac{J - B\beta'}{B\beta'}; \text{ and } t = 100 \frac{J - B\beta'}{B\beta'}, \text{ or, finally,}$$

$$\frac{t - T_0}{100} = \frac{b\beta'}{B\beta'}.$$

Experiments on any one substance determine  $T_0$ . Its value is probably nearer to 274 than to any other integer.

172. Referring again to the diagram of § 168, let  $H_1, H, H_0$  be the quantities of heat which must be supplied to the

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<sup>1</sup> *Trans. R.S.E.*, May 1854.

body in expanding at constant temperatures  $T_1$ ,  $t$ ,  $T_0$  respectively from  $B$  to  $B''$ , from  $b$  to  $b''$ , and from  $\beta$  to  $\beta''$ . Our definition of temperature (§ 170) gives at once

$$\frac{H_1}{T_1} = \frac{H}{t} = \frac{H_0}{T_0}.$$

Hence there is a quantity, characteristic of the substance at all points on the same adiabatic line, such that, if  $\phi_0$  be its value along  $Bb\beta$ , and  $\phi$  its value along  $B''b''\beta''$ , we may write

$$\phi - \phi_0$$

as the common value of the three equal quantities above.

The absolute value of  $\phi$  for any particular adiabatic line must be regarded as arbitrary. We may therefore assume  $\phi = 0$  for the adiabatic which passes through the point of the diagram corresponding to the standard state of the substance.

**173.** The lines in the diagram of § 168 have thus the equations

$$t = \text{const.} \quad (\text{Isothermal.})$$

$$\phi = \text{const.} \quad (\text{Adiabatic.})$$

and it is clear that, while  $t$  and  $\phi$  may be treated as absolutely independent of one another, the volume, pressure, energy, etc., of the working substance are determined when  $t$  and  $\phi$  are given.

These remarks will enable the student to follow easily some parts of the analysis below—especially the investigations of Rankine and Clausius.

**174.** Simple as these geometrical processes are, the following analytical method is really simpler. Let the quantity ( $dq$ ) of heat required to alter the volume ( $v$ ) and temperature ( $t$ ) of unit mass of the working substance by infinitesimal quantities  $dv$  and  $dt$  be represented by

$$dq = Mdv + Ndt \quad (1).$$

Then the whole external work done by the substance,

less the dynamical equivalent of the heat supplied, is

$$p dv - J(M dv + N dt) \quad (2),$$

if  $p$  be the pressure of the working substance.<sup>1</sup>

Hence the whole loss of energy during any series of changes is

$$\int [(p - JM) dv - JN dt] \quad (3),$$

where, in order that one definite cycle may be represented,  $t$  and  $v$  must be assigned in terms of some one independent variable, such as the *time*.

Again, the first law of thermodynamics shows us that in any *complete cycle* of operations the external work done is equal to the heat which has disappeared, *i.e.* there is no loss of energy: so that the above integral (3) must vanish for a complete cycle *whatever be the relation* between  $v$  and  $t$ . Hence the quantity under the integral sign must be the complete differential of a function of the two independent variables  $v$  and  $t$ . This gives at once the condition

$$\begin{aligned} \frac{d}{dt}(p - JM) &= -J \frac{dN}{dv} \\ \text{or } \frac{dp}{dt} &= J \left( \frac{dM}{dt} - \frac{dN}{dv} \right) \end{aligned} \quad (4),$$

which is the complete analytical statement of the first law.

By § 162 we see that the second law may put in the form

$$\frac{dp}{dt} = \frac{JM}{t} \quad (5),$$

using the definition of temperature as in § 170.

<sup>1</sup> That  $p dv$  is the work done during the change of volume  $v$  to  $v + dv$  at pressure  $p$  may be proved as follows. Let  $n$  be the infinitesimal displacement of the bounding surface of the fluid at any point, measured in the direction of the normal, then the whole increase of volume is

$$dv = \iint n dS$$

where  $dS$  is an element of the bounding surface. But, because the pressure is the same throughout (§ 154) we have from this equation

$$p dv = p \iint n dS = \iint n p dS.$$

The latter form expresses the whole work done by the outward force ( $p dS$ ) on each element of the surface, acting through the space ( $n$ ) by which that element is displaced in the direction of the force.

These equations (4) and (5), contain the whole theory. Thus it appears that the expression

$$\frac{dM}{dt} - \frac{dN}{dv}$$

does not in general vanish, and therefore that, in (1),  $dq$  is not a complete differential of a function of two independent variables  $v$  and  $t$ .

But it is known that there is always what is called an *Integrating Factor* in such cases. Call it  $\Theta$ . Then to find it we have

$$\Theta dq = \Theta(Mdv + Ndt)$$

Whence

$$\frac{d}{dt}(\Theta M) = \frac{d}{dv}(\Theta N).$$

Hence we have

$$M \frac{d\Theta}{dt} - N \frac{d\Theta}{dv} = \Theta \left( \frac{dN}{dv} - \frac{dM}{dt} \right) = - \frac{\Theta}{J} \frac{dp}{dt} =$$

(by (5) i.e. by second law)

$$= - \frac{\Theta M}{t}.$$

As there is no necessary relation in general between  $M$  and  $N$

let

$$\frac{d\Theta}{dv} = 0.$$

Then

$$\frac{d\Theta}{dt} = - \frac{\Theta}{t} \text{ and } \Theta \propto \frac{1}{t}.$$

Hence

$$\frac{dq}{t} \text{ is a complete differential,}$$

and it is easy to see that its value is  $d\phi$ , where  $\phi$  has the meaning assigned in § 172.

This is another way of writing in symbols the Second Law.

**175.** We now proceed to the investigation of the quantity of heat required, under different circumstances as to temperature, for the production of a given amount of work.

Consider an engine whose range is finite to be made up of an infinite number of engines with infinitesimal range, and let  $q + dq$  and  $q$  be the quantities of heat taken in and

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given out by that in which the working substance is at the temperature  $t$ .

By the first law the work done is

$$Jdq.$$

By the second law it is (§ 161)

$$JCqdt,$$

or, by § 170,

$$\frac{J}{t}qdt.$$

Hence, by equating these values of the same quantity, given by the two laws separately, we have

$$\frac{dq}{q} = \frac{dt}{t}.$$

Hence  $q$  is proportional to  $t$ , or

$$q = At$$

where  $A$  is some constant.

Thus in a reversible engine with finite range, where  $q$  units of heat are taken in at the temperature  $t$ , and  $q_0$  given out at the lower temperature  $t_0$ , we have (as in § 171)

$$\frac{q}{t} = \frac{q_0}{t_0} = A;$$

$$\text{or,} \quad \frac{q}{t} - \frac{q_0}{t_0} = 0. \quad (6).$$

The work done is, of course,

$$J(q - q_0),$$

and this, by means of (6) can be at once put in the form

$$Jq \frac{t - t_0}{t},$$

so that, as in § 54, the percentage, of the heat taken from the source, which is realised as useful work is the range of the engine divided by the higher absolute temperature. This pure numerical ratio is sometimes called the *Efficiency*



of the engine; but the *Duty*, the term more commonly employed in the vernacular of engineers, is the number of foot-pounds of work obtained from each pound of coal consumed, a considerably more complex quantity.

176. The important equation (6) was extended by its discoverer<sup>1</sup> as follows. If a material system experience a continuous action, or a complete cycle of operations, of a perfectly reversible kind, the quantities of heat which it takes in at different temperatures are subject to a homogeneous linear equation, of which the co-efficients are the reciprocals of these temperatures. If  $q_n$  be the heat taken in at temperature  $t_n$  (to be reckoned as negative when heat is given out), this is expressed by the formula

$$\frac{q_1}{t_1} + \frac{q_2}{t_2} + \frac{q_3}{t_3} + \dots + \frac{q_n}{t_n} = 0,$$

$$\text{or } \sum \frac{q}{t} = 0. \quad (7).$$

To prove this, conceive now, in addition to this given system, an engine *emitting* a quantity  $q_1$ , of heat at temperature  $t_1$ , and taking in the corresponding quantity  $\frac{t_2}{t_1}q_1$  at temperature  $t_2$ ; then an engine emitting the quantity  $\frac{t_2}{t_1}q_1 + q_2$  at  $t_2$ , and taking in the corresponding quantity  $t_3\left(\frac{q_1}{t_1} + \frac{q_2}{t_2}\right)$  at temperature  $t_3$ ; another emitting  $t_3\left(\frac{q_1}{t_1} + \frac{q_2}{t_2}\right) + q_3$  at  $t_3$ , and taking in the corresponding quantity

$$t_4\left(\frac{q_1}{t_1} + \frac{q_2}{t_2} + \frac{q_3}{t_3}\right) \text{ at } t_4;$$

and so on. These  $n-2$  engines constitute a material

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<sup>1</sup> *Trans. R.S.E.* (May) 1854. See also *Proc. R.S.E.*, Dec. 1851, or *Phil. Mag.*, 1852; *Mechanical Theory of Thermo-electric Currents*, Eq. (b).

system, which causes, by reversible operations, an emission of heat  $q_1$  at temperature  $t_1$ ,  $q_2$  at  $t_2$ , and  $q_{n-2}$  at  $t_{n-2}$ ; and taking in

$$t_{n-1} \left( \frac{q_1}{t_1} + \frac{q_2}{t_2} + \dots + \frac{q_{n-2}}{t_{n-2}} \right)$$

at temperature  $t_{n-1}$ . Now this system, along with the given one, constitutes a complex system, causing, on the whole, neither absorption nor emission of heat at the temperatures  $t_1$ ,  $t_2$ , etc., or at any other temperatures than  $t_{n-1}$ ,  $t_n$ ; but giving rise to an absorption or emission equal to

$$\pm \left[ t_{n-1} \left( \frac{q_1}{t_1} + \frac{q_2}{t_2} + \dots + \frac{q_{n-2}}{t_{n-2}} \right) + q_{n-1} \right]$$

at  $t_{n-1}$ , and an emission or absorption equal to  $\pm q_n$  at  $t_n$ . This complete system fulfils the criterion of reversibility; and having only two temperatures at localities where heat is taken in or given out, is subject to the second law as expressed in (6): so that we must have

$$\frac{q_n}{t_n} + \frac{1}{t_{n-1}} \left[ t_{n-1} \left( \frac{q_1}{t_1} + \frac{q_2}{t_2} + \dots + \frac{q_{n-2}}{t_{n-2}} \right) + q_{n-1} \right] = 0,$$

$$\text{or } \frac{q_1}{t_1} + \frac{q_2}{t_2} + \dots + \frac{q_{n-1}}{t_{n-1}} + \frac{q_n}{t_n} = 0,$$

which may be considered as a general expression of the second law of thermodynamics. The first law has the corresponding expression

$$W + J(q_1 + q_2 + \dots + q_{n-1} + q_n) = 0,$$

where  $W$  denotes the aggregate amount of work spent in producing the operations.

For convenience of reference we may repeat these formulae in the following concise form—

$$W + J \sum q = 0 \quad (8)$$

$$\Sigma \frac{q}{t} = 0 \quad (7).$$

If the engine or system be not reversible, this last equation is no longer true. In such a case, the left-hand member is obviously a *positive* quantity, if we consider heat taken in as positive, and suppose the engine to be one in which work is produced from heat.

177. If we suppose the temperatures of different parts of the working substance to alter gradually during the process, it is obvious that we must write (7) in the form

$$\int \frac{dq}{t} = 0 \quad (9).$$

on the supposition that the cycles are reversible. This integral is of remarkable importance in the theory of heat. But, before entering on an examination of it, we may advantageously consider the subject from a somewhat different point of view.

178. The real dynamical value of a quantity,  $dq$ , of heat is  $\int dq$ , whatever be the temperature of the body which contains it. But the *practical* value is only (§§ 54, 175)

$$\int \frac{t-t_0}{t} dq$$

where  $t$  is the temperature of the hot body, and  $t_0$  the lowest available temperature. This value may be written in the form

$$\int dq - \int t_0 \frac{dq}{t}.$$

Hence, in any cyclical process whatever, if  $q_1$  be the whole heat taken in, and  $q_0$  that given out, the practical value is

$$J(q_1 - q_0) - \int t_0 \frac{dq}{t}.$$

Now, if the cycle be *reversible*, the practical value is

$$J(q_1 - q_0)$$

by the first law; so that, in this particular case (at least unless  $t_0=0$ ),

$$\int \frac{dq}{t} = 0.$$

But in general this integral has a finite positive value, because in non-reversible cycles the practical value of the heat is always less than

$$J(q_1 - q_0).$$

Hence the amount of heat lost needlessly, *i.e.* otherwise than to the refrigerator, or in producing work, is

$$t_0 \int \frac{dq}{t} .^*$$

This is Thomson's<sup>1</sup> expression for the amount of heat *dissipated* during the cycle. It is, of course, an immediate consequence of his important formula for the work of a perfect engine (§ 175).

[It is very desirable to have a word to express the *Availability* for work of the heat in a given magazine; a term for that possession, the waste of which is called *Dissipation*.]

179. If an irregularly heated body be enclosed in a non-conducting envelop, there will be dissipation by thermal conduction, as all parts of the body gradually arrive at a common temperature. Thomson in 1853<sup>2</sup> gave a second investigation of the amount of work which can be obtained from such a body by means of perfect thermodynamic

\* We have used the notation  $dq$  for an element of heat, although  $q$  itself is not exactly defined, because a change of notation from that of the preceding sections might perplex the student. It would be better, perhaps, to write  $\frac{dq}{d\tau} d\tau$ , where  $\tau$  represents *time*, instead of  $dq$ ; or to make the temperature,  $t$ , itself the independent variable in the integral, as is done in the following section.

<sup>1</sup> *Phil. Mag. and Proc. R.S.E.*, 1852, 'On a Universal Tendency in Nature to Dissipation of Energy.'

<sup>2</sup> 'On the Restoration of Mechanical Energy from an unequally heated Space.'—*Phil. Mag.*, Feb. 1853.

engines employed to reduce all its parts to the same temperature. His formulæ, without material alteration, can be given (as below) in a much more simple form.

Let  $dm$  be an element of the mass of the irregularly heated body,  $t$  the temperature of the element, and  $c$  its specific heat. Let  $T$  be the temperature to which the whole body can be brought by means of perfect engines, so that all the heat lost is converted into work. Then we must have no heat on the whole given to an auxiliary body at temperature  $T$ , which we may suppose employed as source or condenser for the engine according as we are dealing with a portion of the body below or above the temperature  $T$ . This condition gives us at once the equation

$$0 = \int dm \int_T^t c dt \frac{T}{t}$$

where the final integration extends through the whole mass of the body. This equation gives us the means of determining  $T$ . Similarly, the work obtained is

$$W = J \int dm \int_T^t c \frac{t-T}{t} dt = J \int dm \int_T^t c dt$$

by the preceding equation.

180. These formulæ are greatly simplified if we assume the specific heat to be independent of the temperature, for we have

$$0 = \int c dm \log \frac{t}{T}$$

or

$$T = e^{\frac{\int c dm \log t}{\int c dm}},$$

and

$$W = J \int c dm (t - T).$$

181. We may still farther simplify the equations by assuming that the body is homogeneous, or that  $c$  is the same for every element, and, as before, independent of the temperature. Even if the body be heterogeneous, yet if the

specific heat do not depend on the temperature, we may put for the portion of any one kind of matter which has the same temperature throughout,

$$m_1 = \int c dm.$$

and then  $m_1$ , etc., are the water equivalents of these portions. Let, then, a mass  $m_1$  of the body be given at temperature  $t_1$ , etc., and we have

$$T = e^{\frac{\sum(m \log t)}{\sum m}} = (t_1^{m_1} t_2^{m_2} t_3^{m_3} \dots)^{\frac{1}{\sum m}},$$

$$W = Jc[\Sigma(mt) - T\Sigma m].^1$$

When there are but two equal masses, at temperatures  $t$  and  $t'$ , the values are

$$T = \sqrt{tt'}$$

$$W = Jcm(t + t' - 2\sqrt{tt'}) = Jcm(\sqrt{t} - \sqrt{t'})^2.$$

Such results as this may of course be easily obtained by a much simpler process than the general one adopted above.

182. We may now speak of the Available Energy (A. E.) of a single unequally heated body; and of the mutual A. E. of the parts of a system. And the following theorems are easily proved:—

The A. E. of a system is the sum of the A. E. of its parts, together with their mutual A. E., when their individual A. E. have been exhausted.

The mutual A. E. of any number of equal masses (whose specific heats do not vary with temperature) is proportional to the excess of the arithmetic, over the geometric, mean of their absolute temperatures.

The A. E. of the universe tends continually to zero.

183. Clausius,<sup>1</sup> who published results equivalent to those of § 176 at a somewhat later date, calls such a term as  $\frac{q}{t}$  the *equivalence-value* of the transformation of the quantity  $q$

<sup>1</sup> Tait, *Proc. R.S.E.* 1867-8.

<sup>2</sup> *Pogg. Ann.* (December) 1854.

of heat into work, or *vice versa*, at the temperature  $t$ . And then equation (6) becomes the *theorem of the equivalence of transformations*: which he expresses in words as follows:—If two transformations which, without necessitating any other permanent change, can mutually replace one another, be called equivalent, then the generation of the quantity of heat  $q$  of the temperature  $t$  from work has the equivalence-value

$$\frac{q}{t},$$

and the passage of the quantity of heat  $q$ , from the temperature  $t_1$  to the temperature  $t_2$ , has the equivalence-value

$$q\left(\frac{1}{t_2} - \frac{1}{t_1}\right).$$

Instead of the absolute temperatures as above (§ 170) defined, Clausius introduces an unknown function,  $T$ , of the temperature; and, at the end of his paper, gives reasons, (§ 48) for considering it probable that  $T$  is simply the absolute temperature as measured on a perfect gas thermometer. He does not seem (at least in any of his earlier papers) to adopt or even refer to the *absolute* definition of temperature. This is one instance illustrating the general remark quoted in § 50 above from Thomson.

In his later papers Clausius calls by the name *Entropy* the quantity

$$\phi, \text{ or } \int_0^1 \frac{dq}{t}$$

integrated from the standard state (0) to the actual state (1). There is a difficulty about its exact definition, as will be seen from § 172 and footnote to § 178.

184. From the equation

$$\int \frac{dq}{t} = 0, \quad (9.)$$

or, as it may be written,

$$\int \frac{Mdv + Ndt}{t} = 0,$$

we may of course at once reproduce the formula (5) of (§ 174) by introducing again the first law. For the equation indicates that the quantity under the integral sign is, as already shown in § 174, the complete differential of a function of two independent variables, so that

$$\frac{d}{dt}\left(\frac{M}{t}\right) = \frac{d}{dv}\left(\frac{N}{t}\right)$$

which gives

$$\frac{dN}{dv} = \frac{dM}{dt} - \frac{M}{t},$$

$$\text{or} \quad \frac{1}{J} \frac{dp}{dt} = \frac{dM}{dt} - \frac{dN}{dv} = \frac{M}{t}.$$

From these we obtain

$$\frac{dN}{dv} = \frac{1}{J} \left\{ \frac{d}{dt} \left( t \frac{dp}{dt} \right) - \frac{dp}{dt} \right\} = \frac{t}{J} \frac{d^2 p}{dt^2}.$$

185. From (§ 174) it is evident that  $N$  is the *specific heat at constant volume*. To deduce a relation between the two specific heats, let  $K$  be the *specific heat at constant pressure*. Then

$$K dt = M dv + N dt$$

the relation between  $v$  and  $t$  being such that the pressure is constant, a condition which gives us the equation

$$0 = \frac{dp}{dv} dv + \frac{dp}{dt} dt.$$

Eliminating the differentials  $dv$  and  $dt$ , we have

$$K - N = -M \frac{\frac{dp}{dt}}{\frac{dp}{dv}} = -\frac{t}{J} \frac{\left(\frac{dp}{dt}\right)^2}{\frac{dp}{dv}} \quad (10).$$



186. In the case of the ideal perfect gas, we have, by the law of Charles, combined with that of Boyle,

$$pv = \frac{p_0 v_0}{t_0} t = Rt \quad (11).$$

suppose: so that  $\frac{dp}{dv} = -\frac{p}{v}$ ,

and  $\frac{dp}{dt} = \frac{p}{t} = \frac{JM}{t}$ , by (5)

so that  $p = JM$ .

For such a substance, therefore, we have

$$K - N = \frac{t \frac{p^2}{t^2}}{J \frac{p}{v}} = \frac{pv}{Jt} = \frac{R}{J},$$

an absolute constant.

This property of permanent gases was arrived at by Carnot in his original work. It gives by the equation preceding  $(K - N) p = RM$ .

Also, by (§ 184),

$$\frac{dN}{dv} = 0 \quad (12).$$

If the gas expand or be compressed at constant temperature

$$dq = Mdv = \frac{p dv}{J} = \frac{dw}{J},$$

that is, the whole work spent is converted into heat, or the whole heat supplied is converted into work.

If it have its volume changed in a non-conducting vessel

$$0 = Mdv + Ndt.$$

Taking  $v$  and  $p$  as independent variables this may be written

$$\begin{aligned} 0 &= RMdv + Nd(pv) \\ &= Kp dv + Nvd p, \end{aligned}$$

or  $p^N v^K = \text{const.} \propto \epsilon^\phi,$

as the reader may easily prove for himself. This is the relation between the pressure and volume of air in a sound-wave.

187. We may now take some of Thomson's more general applications of the dynamical theory to the effects of compression and distortion of bodies as regards the heat developed (§ 57). For this purpose we must express the compressibility, etc., in terms of the alterations produced, and the forces producing them.

188. If a substance, at pressure  $p$  and volume  $v$ , be compressed by an increase of pressure,  $\delta p$ , to volume  $v + \delta v$ , the temperature being kept constant, the compressibility is

$$-\frac{\delta v}{v} \cdot \frac{1}{\delta p}.$$

Hence, if  $\kappa$  represent the reciprocal of the compressibility, which may be called elasticity of volume, or cubical elasticity,

$$\kappa = -v \frac{dp}{dv}. \quad (13).$$

In the ideal perfect gas this is  $p$ . Hence arises the confusion as to the meaning of the term 'elasticity.' For the co-efficient of elasticity of volume is proportional to  $p$  whether  $t$  or  $\phi$  be constant. In many books the elasticity of a gas is *merely another name* for its pressure.

189. Again, if  $e$  be the co-efficient of cubical dilatation by heat at constant pressure,

$$\frac{\delta v}{v} = e \delta t.$$

$$\text{Thus} \quad e = \frac{1}{v} \frac{dv}{dt} = -\frac{1}{v} \frac{\frac{dp}{dt}}{\frac{dp}{dv}} = \frac{1}{\kappa} \frac{dp}{dt} \quad (14).$$

Thus in the ideal perfect gas  $e = \frac{1}{t}$ .

190. If we substitute, in terms of these quantities, the values of the differential co-efficients of  $p$ , the general equations of §§ 184, 185 take the more easily intelligible forms

$$J \frac{dN}{dv} = \frac{d}{dt}(\kappa e t) - \kappa e = t \frac{d}{dt}(\kappa e) = t \frac{d^2 p}{dt^2} \quad (15),$$

$$J(K - N) = tv(\kappa e)e \quad (16).$$

$$JM = t(\kappa e) \quad (17).$$

Of these, the first gives a singular relation between the rate at which the specific heat at constant volume is altered by a change of volume at constant temperature, and the rate at which the pressure at constant volume alters with the temperature. The third shows the amount of heat developed by compression when the temperature is kept constant. But it may be usefully applied, in connection with the second, to find the change of temperature produced by compression when a substance is enclosed in a non-conducting vessel. For, if  $\delta t$  be the change of temperature due to the compression  $\delta v$ , we have

$$N\delta t = M\delta v,$$

$$\text{or} \quad \delta t = \frac{t \cdot \kappa e}{JN} \delta v$$

which may also be written

$$\delta t = \frac{t \cdot \kappa e}{JK - t \cdot \kappa e \cdot v e} \delta v.$$

From any of these expressions we see that when a substance contracts as its temperature rises (as is the case, for instance, with water between its freezing-point and its point of maximum density), its temperature is lowered by sudden compression. For in such a substance  $e$  is negative.

Another useful formula, also given by Thomson,<sup>1</sup> and immediately deducible from the above, is

$$\delta t = \frac{tev}{JK} \delta p. \quad (18).$$

<sup>1</sup> *Proc. R. S.* 1857, or *Phil. Mag.* 1858, i. 541. See also *Comptes Rendus*, Oct. 1864, for another elementary investigation.

191. Consider next the working substance to consist of a mixture of a mass  $1-x$  of some body in one molecular state, and a mass  $x$  of the same in another state, at the same temperature, but containing more latent heat. These may be, for instance, water and saturated steam, or ice and water.

Let the volumes of unit mass of the body in these two states be respectively  $V$  and  $V_1$ , their specific heats (that is to say, the quantity of heat required to raise the temperature of unit mass of either form of the substance one degree, under the condition that the two forms remain in equilibrium during the process)  $c$  and  $c_1$ ,  $L$  the latent heat of unit mass in the second state, and  $p$  the common pressure which depends solely on the temperature and on the nature of the body.

Then, if  $v$  be the joint volume,

$$V(1-x) + V_1x = v \quad (19).$$

Also,  $M$  and  $N$  having the same meaning as in § 174,

$$Mdv = L \frac{dx}{dv} dv,$$

and

$$Ndt = c(1-x)dt + c_1xdt + L \frac{dx}{dt} dt.$$

But, by differentiation of (19) we have

$$\frac{dx}{dv} = \frac{1}{V_1 - V} \quad (20)$$

$$(V_1 - V) \frac{dx}{dt} + (1-x) \frac{dV}{dt} + x \frac{dV_1}{dt} = 0. \quad (21).$$

Combining these with the preceding equations, we have

$$M = \frac{L}{V_1 - V} \quad (22).$$

and

$$N = c(1-x) + c_1x - L \frac{(1-x) \frac{dV}{dt} + x \frac{dV_1}{dt}}{V_1 - V} \quad (23).$$

But we have (§ 174)

$$\frac{dp}{dt} = J \left( \frac{dM}{dt} - \frac{dN}{dv} \right)$$

and, by (22) and (23), this becomes

$$\frac{dL}{dt} + c - c_1 = \frac{V_1 - V}{J} \frac{dp}{dt} \quad (24)$$

a result from which  $x$  has of course disappeared.

Also, we have, by the expression for Carnot's function, viz. :—

$$JC = \frac{1}{M} \frac{dp}{dt},$$

$$JC = \frac{V_1 - V}{L} \frac{dp}{dt} \quad (25)$$

or, by (§ 170),

$$\frac{J}{t} = \frac{V_1 - V}{L} \frac{dp}{dt} \quad (26).$$

Substituting in (24) we obtain, finally,

$$\frac{dL}{dt} + c - c_1 = \frac{L}{t} \quad (27).$$

**192.** These equations give us among other results the means of determining the effect of pressure on the melting, or boiling, point of a substance.

Thus

$$dt = \frac{V_1 - V}{JL} t dp$$

so that an increase of pressure raises the melting, or boiling, point if  $V_1$  is greater than  $V$  (as it is in the case of water and steam), but lowers it where (as in ice and water)  $V_1$  is less than  $V$  (§ 55).

By means of an equation identical with (24), Clausius

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obtained the result that the latent heat of water is diminished by pressure.

And Regnault's experiments have shown that  $\frac{L}{t}$  for steam is greater than  $\frac{dL}{dt} + c$ , so that (27) gives us at once the important result of Rankine and Clausius (§ 51), as to superheated steam, in the form  $c_1$  is negative.

For other curious applications of the fundamental formulæ, to the solution of salts and gases in water, etc., the reader is referred to a valuable paper by Kirchhoff.<sup>1</sup>

193. The amount of heat which must be communicated to a body, kept at constant temperature  $t$ , so as to increase its volume from  $v$  to  $v + dv$ , is (§ 174)

$$dq = Mdv.$$

Hence, if the body expand from  $v'$  to  $v$  (still at constant temperature  $t$ ), the whole heat communicated must be

$$q = \int_{v'}^v Mdv.$$

Substituting from (5) the value of  $M$ , in terms of Carnot's function, this becomes

$$q = \frac{t}{J} \int_{v'}^v \frac{dp}{dt} dv = \frac{t}{J} \frac{d}{dt} \int_{v'}^v p dv.$$

If we put  $w$  for the external work done during the expansion at constant temperature from  $v'$  to  $v$ ,

$$w = \int_{v'}^v p dv.$$

Hence,

$$q = \frac{t}{J} \frac{dw}{dt}.$$

If the substance be such that the whole of the heat communicated is spent in external work, when the body expands so as to remain at a constant temperature, or if the heat

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<sup>1</sup> *Pogg. Ann.* 1858, 'Ueber einen Satz der mechanischen Wärmetheorie, und einige Anwendungen desselben.'

given out when it is compressed and kept at a constant temperature be the equivalent of the work spent in compressing it (*i.e.* if Séguin and Mayer's hypothesis be assumed), we must have

$$q = \frac{w}{J}.$$

Hence, for such a substance,

$$\frac{dw}{dt} = \frac{w}{t} = \text{constant}.$$

$$\text{or } \frac{dq}{dt} = \frac{q}{t} = \text{constant}.$$

194. When a gas is forced through a porous plug, we might suppose it to descend from one given pressure to another in such a way that the work which it does during the change is entirely converted into heat by fluid friction. The quantity of heat developed by the operation must therefore be the excess of heat due to the work spent on the gas, over that which is required to enable it to expand from the higher to the lower pressure without considerable change of temperature. The former is  $\frac{w}{J}$ , the latter, as we have just seen, is  $\frac{t}{J} \frac{dw}{dt}$ . Hence, the whole heat developed is

$$q = \frac{1}{J} \left( w - t \frac{dw}{dt} \right),$$

and vanishes, as it ought, for the ideal perfect gas, in which

$$\frac{w}{t} = \frac{dw}{dt}.$$

In Thomson's experiment (§ 63), the work done is not wholly expended in fluid friction, so that the equations applicable to it involve additional terms depending on the initial and final values of  $p v$ .

195. A very clear insight into the meaning of the fundamental formula (§ 174) may be obtained by seeking (as was

first done by Thomson<sup>1</sup>) an expression for the *Energy*, which a substance contains in virtue of its state as to volume and temperature. [These two quantities are, in general, sufficient to define completely, at any instant, the state of a given quantity of the substance, as from them the pressure, etc., may be deduced from tables, or from empirical laws founded on experiment. To consider the exceptional cases of the so-called 'triple point,' etc., would require more detail than we can give.] The work done may consist wholly or partially of actual expansion against resistance, or in the communication of heat, whether by conduction, convection, or radiation, to surrounding bodies. And the whole energy in the body must be diminished by the quantity thus given off. Thus we see that, if the initial and final states be given, the quantity of energy parted with or supplied is perfectly determinate. In general it is only such *changes* in the intrinsic energy of a body that can be measured; the whole amount present is unknown, but cannot be infinite in a finite quantity of matter. We must therefore suppose  $E$  to be measured from some particular state, say the standard temperature and pressure—just as  $\phi$  was measured in § 172.

196. When a substance, by the application of heat, is made to expand from  $v$  to  $v+dv$ , and to rise in temperature from  $t$  to  $t+dt$ , the amount of heat supplied is (§ 174)

$$Mdv + Ndt;$$

and the amount of work done on external bodies is

$$p dv,$$

Hence the amount by which the energy  $E$ , present in the body, has been increased is

$$dE = J(Mdv + Ndt) - p dv. \quad (28).$$

We have already seen (§ 174) that this expression is a com-

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<sup>1</sup> *Trans. R. S. E.*, 1851, 'On the Quantities of Mechanical Energy contained in a Fluid in different states.'



plete differential of two independent variables, in consequence of the first law of thermodynamics. Hence we may write

$$\left. \begin{aligned} \frac{dE}{dv} &= JM - p, \\ \frac{dE}{dt} &= JN \end{aligned} \right\} \quad (29).$$

and, by eliminating  $E$  by differentiation, we obtain again the results of § 174.

197. We may put the equation (28) into many other forms, some of which are of considerable use. Thus, by (5) we have

$$dE = \left( t \frac{dp}{dt} - p \right) dv + JN dt$$

and, putting  $w = \int v p dv$  as in (§ 193), and arranging so as to make the first term a complete differential,

$$dE = d \left( t \frac{dw}{dt} - w \right) + \left( JN - t \frac{d^2 w}{dt^2} \right) dt \quad (30).$$

The last term therefore is obviously a complete differential, from which we see that

$$JN - t \frac{d^2 w}{dt^2} = T,$$

where  $T$  is some function of  $t$  only. Differentiating with respect to  $v$ , we reproduce the formula of (§ 184), *i.e.*,

$$J \frac{dN}{dv} - t \frac{d^2 p}{dt^2} = 0.$$

198. By integrating the first equation of (29), or directly by (30)

$$E = t \frac{dw}{dt} - w + \int T dt$$

so that the energy of the ideal perfect gas, for which

$$t \frac{dw}{dt} - w = 0,$$

depends solely upon its temperature.

199. Clausius has adopted an extremely different mode of attacking questions as to the effect produced by heat upon a substance. The following sections will give the reader an idea of the nature of his investigations, for the complete development of which we must refer to his works.<sup>1</sup>

If a quantity  $dq$  of heat be communicated to a body, part of it,  $dH$  suppose, is expended in increasing the quantity of thermometric heat present in the body, the remainder being expended in external, and in what he calls internal, work. Hence, if  $W$  denote the whole work done, whether internal or external, we have

$$dq = dH + \frac{1}{J} dW.$$

200. Now Clausius defines as the *Disgregation* the quantity  $Z$ , where

$$t dZ = \frac{1}{J} dW$$

thus assuming that the work which heat can perform is proportional to the absolute temperature, and that increase of disgregation is the action by which heat does work, so that the sum of the elements of work done internally and externally is proportional to the corresponding increment of the disgregation multiplied by the absolute temperature.

By the above equations we have

$$\begin{aligned} dq &= dH + t dZ, \\ \text{or } \int \frac{dq}{t} &= \int \frac{dH}{t} + \int dZ. \end{aligned}$$

Now by (9) of § 177, we see that in a reversible cyclical process the left-hand member of the equation vanishes. Also the term  $\int dZ$  must vanish, since the substance has been restored to its original state. Hence we see that we must have

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<sup>1</sup> *Abhandlungen über die mechanische Wärmetheorie.* Leipsic, 1864-7

$$\int \frac{dH}{t} = 0.$$

From this equation Clausius infers that  $H$  is a function of  $t$ , and therefore that *the temperature of a body depends solely on the amount of actual heat which it contains, and not upon the arrangement of its molecules.*

In this form, Clausius' result seems to us to be by no means evident. In fact the very definition of  $Z$  makes it a function of  $t$  alone. And it is pure assumption to state that  $\frac{dq}{t}$ , which is undoubtedly a complete differential in the case supposed, is necessarily capable of being represented as the sum of two complete differentials of the kinds specified above. The source of all this sort of speculation, which is as old as the time of Crawford and Irvine—and which was to some extent countenanced even by Rankine—is the assumption that bodies must contain a certain quantity of actual, or thermometric, heat. We are quite ignorant of the condition of energy in bodies generally. We know how much goes in, and how much comes out, and we know whether at entrance or exit it is in the form of heat or work. But that is all.

201. Taking Clausius' expression for granted, however, it may be interesting to inquire how the so-called internal work is to be determined. Let  $w$  be the external work,  $w'$  the internal, then

$$W = w + w'.$$

And, as we have

$$dw = p dv, \quad dw' = \frac{dw'}{dt} dt + \frac{dw'}{dv} dv,$$

the expression (§ 200) for the disgregation becomes

$$Jt dZ = \frac{dw'}{dt} dt + \left( \frac{dw'}{dv} + p \right) dv.$$

Hence  $Jt \frac{dZ}{dt} = \frac{dw'}{dt}$ ,  $Jt \frac{dZ}{dv} = \frac{dw'}{dv} + p$ .

Eliminating  $w'$  by differentiation we get

$$\begin{aligned}\frac{dp}{dt} &= J \left[ \frac{d}{dt} \left( t \frac{dZ}{dv} \right) - \frac{d}{dv} \left( t \frac{dZ}{dt} \right) \right] \\ &= J \frac{dZ}{dv}.\end{aligned}$$

Hence

$$JdZ = \frac{1}{t} \frac{dw'}{dt} dt + \frac{dp}{dt} dv,$$

or, eliminating  $Z$ ,

$$\frac{dw'}{dv} = t \left( \frac{dp}{dt} - \frac{p}{t} \right).$$

Compare § 194.

202. Rankine obtains a result differing from the penultimate equation above merely in the annulling of the first term on the right-hand side, which, as Clausius allows, can only exist in the case of a substance which is incapable at some temperatures of passing into the state of a perfect gas. Rankine refers to the well-known *smell* of such substances as iron, copper, tin, zinc, and lead, as showing that, at low temperatures, they pass into the state of vapour or gas. Why not, then, into the perfectly gaseous condition?

203. From Rankine's point of view we may write

$$dq = Ndt + t dF,$$

where  $N$  has the same value as in §§ 174, 185, and  $F$  is what he calls the 'Metamorphic Function'; while the 'Thermodynamic Function' is

$$\phi = \int \frac{dq}{t}.$$

204. The nature of Rankine's investigations<sup>1</sup> may be thus shown. The state of unit of mass of a substance is in general determined by the values of two variables. In the diagram of energy  $p$  and  $v$  are used. In most of the text above  $v$  and  $t$  are used, but any two independent functions

<sup>1</sup> *The Steam-Engine and other Prime-movers.* Glasgow, 1866 (2d ed.)

of any two of these are sufficient, that is, any two quantities, each of which has a definite value when  $p$  and  $v$  are given, but which are not themselves connected by any equation involving themselves only. Now

$t$  is such a function of  $p$  and  $v$ .

$\phi$  is another. (See § 172.) To define it—

Operation A. { Let the body in a given state be confined in a non-conducting vessel, and let its pressure and volume be altered till its temperature is  $t_0$ .

Operation B. { Now let its temperature be maintained constant at  $t_0$ , and let it be compressed to volume  $v_0$ , and let it give out  $q$  units of heat in the process; then if  $\phi$  is the value of  $\phi$  in the original state, and  $\phi_0$ , in the state  $v_0, t_0$ ,

$$\phi - \phi_0 = \frac{q}{t_0}.$$

Hence, if  $\phi_0$  is given for a particular state of the substance,  $\phi$  has a perfectly definite value for every other state.

Also,  $dq = td\phi = Mdv + Ndt$

and  $dW = pdv.$

But in any complete cycle

$$\oint dW - \oint dq = 0$$

$$\text{or } \oint pdv - \oint t d\phi = 0$$

so that, by § 196,

$$-pdv + Jtd\phi = dE.$$

Let  $E_0$  be the energy of the body at  $v_0$  and  $t_0$ , and let the body do  $W$  units of work in the two operations  $A$  and  $B$ , and give out  $q$  units of heat in operation  $B$ , then if  $E$  is the original energy,

$$E = E_0 + W + Jq.$$

Thus we have two new functions of the state of the body, or five in all—

$$v, p, t, \phi, E.$$

Among these we have the equations

$$p = -\frac{dE}{dv} \quad (\phi \text{ being constant}),$$

and 
$$t = \frac{1}{J} \frac{dE}{d\phi}, \quad (v \text{ being constant}), \text{ etc.}$$

which give 
$$J\left(\frac{dt}{dv}\right)_{\phi \text{ const.}} = -\left(\frac{dp}{d\phi}\right)_{v \text{ const.}}$$

By the ordinary processes of the differential calculus we may easily vary the form of these relations. For instance

$$d(E + pv) = Jtd\phi + vdp$$

so that 
$$J\left(\frac{dt}{d\phi}\right)_{\phi \text{ const.}} = \left(\frac{dv}{d\phi}\right)_{p \text{ const.}} \text{ etc. etc.}$$

205. These hints may assist the student in the perusal of the works of Rankine and Clausius ; and some such assistance we have felt to be very desirable, as both authors, in the more theoretical and speculative parts of their investigations, are somewhat diffuse and difficult of comprehension.

206. We conclude the chapter with a few investigations taken from Thomson's<sup>1</sup> general paper on the 'Thermo-elastic Properties of Matter.' These refer to any homogeneous solid homogeneously strained.

207. In the first place, we see, by § 176, that however such strain be effected, and through whatever stages the body passes in returning to its first condition, no heat will, on the whole, have been absorbed or given out, provided the temperature has been kept constant throughout the whole operation, and therefore the quantity of heat absorbed for any given change, at constant temperature, does not depend on the way in which that change has been effected. For in this case (7) becomes

$$\Sigma q = 0.$$

208. Hence, if  $x, y, z, \xi, \eta, \zeta$  be any six quantities which

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<sup>1</sup> *Quarterly Math. Journal*, April 1855.

define the state of the body as regards strain,<sup>1</sup> and if  $H$  be the heat absorbed, while the body is made to pass, at constant temperature  $t$ , from  $x_0, y_0, z_0, \xi_0, \eta_0, \zeta_0$ , to  $x, y, z, \xi, \eta, \zeta$ , we must have

$$H = \psi(x, y, z, \xi, \eta, \zeta, t) - \psi(x_0, y_0, z_0, \xi_0, \eta_0, \zeta_0, t).$$

Hence also the corresponding increase of the total energy of the body (§ 196) will be expressed by

$$E - E_0 = \epsilon = \phi(x, y, z, \xi, \eta, \zeta, t) - \phi(x_0, y_0, z_0, \xi_0, \eta_0, \zeta_0, t).$$

where, if  $w$  denote the work done by the applied forces, we have

$$\epsilon = w + JH. \quad (31).$$

Thus, also, the *work* required to strain the body through any given change of state, at a constant temperature, is independent of the succession of strains by which that change is effected.

209. To introduce the consideration of change of temperature, let us take the following reversible cycle of operations, in which (as in § 158) it may be considered as infinitely small.

(I.) Raise the temperature from  $t$  to  $t + dt$ , at the constant state  $x_0, y_0, z_0, \xi_0, \eta_0, \zeta_0$ .

The amount of heat required is

$$\frac{1}{J} \frac{dE_0}{dt} dt.$$

(II.) Change the state of strain from  $x_0, y_0$ , etc., to  $x, y$ , etc., at temperature  $t + dt$ .

The heat required is

$$H + \frac{dH}{dt} dt.$$

(III.) Lower the temperature to  $t$ , at the constant state  $x, y$ , etc.

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<sup>1</sup> Thomson and Tait's *Natural Philosophy*, § 669.

The heat required is

$$-\frac{1}{J} \frac{dE}{dt} dt.$$

(IV.) Restore the original state  $x_0, y_0$ , etc., keeping the temperature at  $t$ .

The heat required is

$$-H.$$

Hence by § 176 we have (neglecting terms in  $(dt)^2$ )

$$\frac{1}{Jt} \frac{d(E_0 - E)}{dt} dt + \frac{H + \frac{dH}{dt} dt}{t + dt} - \frac{H}{t} = 0,$$

or

$$\frac{d}{dt} \left( \frac{H}{t} \right) - \frac{1}{Jt} \frac{d\epsilon}{dt} = 0. \quad (32).$$

Eliminating  $\epsilon$  by means of (31), we have

$$H = -\frac{t}{J} \frac{dw}{dt} \quad (33),$$

as in § 193, remembering that  $w$  has now the negative sign, as it represents work done from without on the body.

Also, substituting this value of  $H$  in (31), we have

$$E - E_0 = \epsilon = w - t \frac{dw}{dt} \quad (34),$$

which is the generalised form of the result of § 198.

210. Various extremely important applications of these equations can easily be given, as will be seen by referring to Thomson's paper, but we confine ourselves to the very simple one which follows.

If the strain be very small, the work required to produce it may be expressed by

$$w = Pdx + Qdy + Rdz + Sd\xi + Td\eta + Ud\zeta, \quad (35),$$

where<sup>1</sup>  $x, y, z$  are taken as rectangular co-ordinates parallel

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<sup>1</sup> Thomson and Tait, § 671.



to the edges of a cubical unit-volume of the solid.  $P$ ,  $Q$ ,  $R$  are the normal pressures on the sides of this cube,  $S$ ,  $T$ ,  $U$  the tangential components of the shearing stress.

Substituting in (33) we have

$$H = -\frac{t}{J} \left( \frac{dP}{dt} dx + \frac{dQ}{dt} dy + \frac{dR}{dt} dz + \frac{dS}{dt} d\xi + \frac{dT}{dt} d\eta + \frac{dU}{dt} d\zeta \right).$$

Hence, as in § 192, if  $P$  [or any other of the co-efficients in (35)] diminish as the temperature increases (so that  $\frac{dP}{dt}$  is negative) cold will be produced (*i.e.* heat must be supplied to keep the temperature constant) during the body's yielding to the effect of the stress denoted by  $P$ ; and heat if it be strained in the opposite way. The reverse will be the case if  $P$ , etc., increase with  $t$ , as is the case, for instance, with gaseous bodies, where  $P$  represents the pressure.

## NOTE A (§ 96).

(a.) The equations of motion of a particle of mass  $m$ , under the action of any system of forces, are

$$m \frac{d^2 x}{dt^2} = X, m \frac{d^2 y}{dt^2} = Y, m \frac{d^2 z}{dt^2} = Z,$$

where  $X, Y, Z$  are the components of the entire force found by resolving it parallel to the several axes of  $x, y, z$ .

From them we at once deduce the *equation of energy*

$$m \left( \frac{dx}{dt} \frac{d^2 x}{dt^2} + \frac{dy}{dt} \frac{d^2 y}{dt^2} + \frac{dz}{dt} \frac{d^2 z}{dt^2} \right) = X \frac{dx}{dt} + Y \frac{dy}{dt} + Z \frac{dz}{dt}$$

If the velocity of  $m$  be called  $v$ , the first integral of this equation may be written

$$\frac{1}{2} m v^2 = \int (X dx + Y dy + Z dz),$$

or, more definitely,  $v_0$  being the velocity of  $m$  when its co-ordinates are  $x_0, y_0, z_0$ ,

$$\frac{1}{2} m (v^2 - v_0^2) = \int_{x_0, y_0, z_0}^{x, y, z} (X dx + Y dy + Z dz).$$

Now the Conservation of Energy requires that the value of  $v$  should be always the same for the same values of  $x, y, z$ ; that is, that the change of kinetic energy in moving from any one position to another should not depend upon the particular path by which that transference is effected. Analytically, this is equivalent to saying that the integration of the right-hand member of the equation must be capable of being effected without any assumed relation or relations between  $x, y$ , and  $z$ . Thus the expression

$$X dx + Y dy + Z dz$$

must be the complete differential of a function of three independent variables. We may therefore write

$$-dV = Xdx + Ydy + Zdz,$$

the negative sign being introduced for reasons of convenience.

We have, therefore,

$$X = -\frac{dV}{dx}, Y = -\frac{dV}{dy}, Z = -\frac{dV}{dz},$$

the differential co-efficients being partial. These show, by the fundamental principles of the Differential Calculus, that we have

$$\frac{dX}{dy} - \frac{dY}{dx} = 0, \frac{dY}{dz} - \frac{dZ}{dy} = 0, \frac{dZ}{dx} - \frac{dX}{dz} = 0;$$

which are the usual analytical conditions for the existence of a complete differential of three independent variables.

Either of the two last groups of equations gives the relations between  $X$ ,  $Y$ ,  $Z$ , which are required by the Conservation of Energy.

(b.) If the only forces acting are such as tend to a fixed centre, and depend on the distance from that centre only, these conditions are fulfilled.

For let  $a$ ,  $b$ ,  $c$  be the co-ordinates of the centre,  $R$  the force it exerts on  $m$  when their mutual distance is  $r$ ; we have

$$r = \sqrt{(x-a)^2 + (y-b)^2 + (z-c)^2},$$

$$X = -R \frac{x-a}{r}, Y = -R \frac{y-b}{r}, Z = -R \frac{z-c}{r}.$$

But

$$r \frac{dr}{dx} = x-a, r \frac{dr}{dy} = y-b, r \frac{dr}{dz} = z-c, \quad \text{so that}$$

$$X = -R \frac{dr}{dx}, Y = -R \frac{dr}{dy}, Z = -R \frac{dr}{dz},$$

and

$$Xdx + Ydy + Zdz = -Rdr.$$

This is a complete differential, because by hypothesis  $R$  is a function of  $r$  only.

(c.) If there be more than one fixed centre it is obvious that we have

$$X = -\Sigma \left( R \frac{dr}{dx} \right), Y = -\Sigma \left( R \frac{dr}{dy} \right), Z = -\Sigma \left( R \frac{dr}{dz} \right) \quad \text{and} \\ Xdx + Ydy + Zdz = -\Sigma(Rdr)$$

every term of which sum is a complete differential.

(d.) When some of the centres are in motion *independently* of the mass  $m$ , the conservation of energy does not necessarily hold good, as it is possible by means of such moving centres to keep  $m$  constantly revolving with ever increasing velocity in some definite path.

(e.) But if the moving centres be themselves masses of the system, and be acted on by  $m$ , and by the fixed centres, only, the conservation of energy is true of the whole moving system. In this form the problem becomes that of several mutually acting particles  $m_1, m_2, \dots$  acted on by fixed centres.

Let the co-ordinates of  $m_1$  be  $x_1, y_1, z_1$ , those of  $m_2, x_2, y_2, z_2$ , etc. Then for the motion of  $m_1$  we have

$$m_1 \frac{d^2 x_1}{dt^2} = -\Sigma \left( R_{1a} \frac{dr_{1a}}{dx_1} \right) - \Sigma \left( S_{1n} \frac{x_1 - x_n}{r_{1n}} \right)$$

with two equations of the same form for  $y_1$  and  $z_1$ . In these equations  $r_{1a}$  is the distance of  $m_1$  from the fixed centre  $a, b, c$ , and  $R_{1a}$  the force exerted by the centre upon  $m_1$ , which is a function of  $r_{1a}$  alone: also  $r_{1n}$  is the distance between  $m_1$  and  $m_n$ , one of the other particles;  $S_{1n}$  the mutual force between them, being a function of  $r_{1n}$  alone.

The corresponding expressions for the motion of  $m_n$  are

$$m_n \frac{d^2 x_n}{dt^2} = -\Sigma \left( R_{na} \frac{dr_{na}}{dx_n} \right) - \Sigma \left( S_{n1} \frac{x_n - x_1}{r_{n1}} \right)$$

with other two similar equations.

Now in the value of  $m_1 \frac{d^2 x_1}{dt^2}$  we have a term

$$-S_{1n} \frac{x_1 - x_n}{r_{1n}},$$

and in

$m_n \frac{d^2 x_n}{dt^2}$  we have the correspond-

ing term

$$-S_{n1} \frac{x_n - x_1}{r_{n1}}.$$

Hence, when we form the expression

$$m_1 \left\{ \frac{dx_1}{dt} \frac{d^2 x_1}{dt^2} + \frac{dy_1}{dt} \frac{d^2 y_1}{dt^2} + \frac{dz_1}{dt} \frac{d^2 z_1}{dt^2} \right\} + m_2 \left\{ \frac{dx_2}{dt} \frac{d^2 x_2}{dt^2} + \dots \right\} + \text{etc.},$$

we find on the right-hand side the terms

$$-S_{1n} \frac{(x_1 - x_n) \frac{dx_1}{dt} + (y_1 - y_n) \frac{dy_1}{dt} + (z_1 - z_n) \frac{dz_1}{dt}}{r_{1n}}$$

and

$$-S_{n1} \frac{(x_n - x_1) \frac{dx_n}{dt} + (y_n - y_1) \frac{dy_n}{dt} + (z_n - z_1) \frac{dz_n}{dt}}{r_{n1}}.$$

Here  $r_{1n}$  and  $r_{n1}$  are the same, being merely the length of the line joining  $m_1$  and  $m_n$ . But

$$S_{n1} = -S_{1n}$$

because action and reaction are equal and opposite. Hence the above terms may be condensed into

$$-S_{1n} \frac{dr_{1n}}{dt},$$

where the differentiation is performed on the supposition that the co-ordinates of  $m_1$  and  $m_n$  both change.

The resulting equation may therefore be written

$$\Sigma m \left( \frac{dx}{dt} \frac{d^2 x}{dt^2} + \frac{dy}{dt} \frac{d^2 y}{dt^2} + \frac{dz}{dt} \frac{d^2 z}{dt^2} \right) = -\Sigma \left( R_a \frac{dr_a}{dt} \right) - \Sigma \left( S \frac{dr}{dt} \right)$$

where  $R_a$  is the force exerted by the fixed centre  $a$ ,  $b$ ,  $c$  upon the particle distant  $r_a$  from it,  $S$  the mutual force between two particles whose mutual distance is  $r$ . Here every term of each of the sums on the right is, separately, a complete differential. The integral may be written

$$\frac{1}{2} \Sigma m v^2 = -V - W,$$

where the left-hand member is the whole kinetic energy of the moving particles; and the right consists of two parts, one due to the fixed centres, the other to the mutual action of the particles.

(f.) The converse, that, if the force acting on a single particle tends to a fixed centre, and if the conservation of energy hold, the force depends only on the distance from that centre, is easily proved. For we must have

$$\frac{1}{2}mv^2 = - \int R dr$$

where it is to be shown that  $R$  is a function of  $r$  only. We have, at once,

$$mv \frac{dv}{dx} = -R \frac{dr}{dx}, \quad mv \frac{dv}{dy} = -R \frac{dr}{dy}; \quad mv \frac{dv}{dz} = -R \frac{dr}{dz}.$$

Hence

$$m \left\{ \frac{d}{dy} \left( v \frac{dv}{dx} \right) - \frac{d}{dx} \left( v \frac{dv}{dy} \right) \right\} = - \left\{ \frac{d}{dy} \left( R \frac{dr}{dx} \right) - \frac{d}{dx} \left( R \frac{dr}{dy} \right) \right\}$$

or

$$0 = \frac{dR}{dx} \frac{dr}{dy} - \frac{dR}{dy} \frac{dr}{dx}$$

with other two equations of the same form—the three forming the usual analytical conditions that  $R$  should be a function of  $r$  only.

(g.) This theorem cannot be extended to any indefinite number of centres: as it is usually possible, by means of centres whose attraction is different in different directions, to build up an arrangement producing on external matter a conservative system of forces only.

(h.) When there is but one fixed centre of force the conservation of energy for a single particle acted on by this centre requires that the force should be exerted in the line joining the particle with the centre, and should depend upon its length only.

For it is obvious that the *relative* position of the particle and the centre depends merely on their *distance*. That is,  $v$  is a function of  $r$  only. Hence

$$\frac{1}{2}mv^2 = -V$$

where  $V$  is a function of  $r$ ; and therefore

$$mv dv = -\frac{dV}{dr} \left( \frac{dr}{dx} dx + \frac{dr}{dy} dy + \frac{dr}{dz} dz \right)$$

But always  $mv dv = X dx + Y dy + Z dz$

so that  $X = -\frac{dV}{dr} \frac{dr}{dx} = -\frac{dV}{dr} \frac{x}{r},$

with similar expressions for  $Y$  and  $Z$ , from which we immediately deduce

$$\frac{X}{x} = \frac{Y}{y} = \frac{Z}{z}.$$

These equations show that the line joining the particle with the centre is the direction of the force.

# NOTE B (§§ III-III3).

(i.) Let  $V$  be the value of the potential at any point  $P$ ,  $V'$  that at any neighbouring point  $P'$ . Then if  $F$  be the mean value, from  $P$  to  $P'$ , of the resolved force along  $PP'$ , we have obviously

$$F.PP' = V' - V.$$

Hence the direction of the whole force is perpendicular to the surface for which  $V$  is constant; for if  $P$  be taken on that surface, the value of the resultant  $F$  along  $PP'$  vanishes.

(j.) The simplest possible instances of electric distribution are afforded by concentric spherical conducting shells, with no external or internal influencing bodies; for each

surface of each shell must then have a uniform distribution of electricity, which may be positive, negative, or zero. It is easy to derive valuable results from this by very simple mathematical processes. We commence by stating two theorems of Newton, upon which the investigations depend.

(1.) The attraction of a uniform spherical shell upon external points is the same as if it were condensed in its centre.

(2.) The attraction of such a shell on internal points is zero.

Hence, if  $V$  be the potential of such a shell at an external point distant  $r$  from its centre,  $V'$  the same at a distance  $r'$  differing but little from  $r$ , and if  $M$  be the mass of the shell, the equation of § (i) becomes

$$\frac{M}{r^2}(r' - r) = V' - V.$$

This is satisfied if we put

$$V = C - \frac{M}{r}.$$

At the surface of the shell we have  $r = R$  and

$$V = C - \frac{M}{R}.$$

Hence the increase of potential in passing from the surface to a distance  $r$  is

$$\frac{M}{R} - \frac{M}{r}.$$

(k.) The potential of a charge  $Q$  of electricity, uniformly distributed over a sphere of radius  $R$ , is therefore

$$\frac{Q}{R}$$

being the work required to remove unit of negative electricity from the surface of the sphere to an infinite distance.

This shows that the potential of any charged conductor may be measured by the quantity of electricity which must be given to a conducting sphere of unit radius, connected



with it by means of a long fine wire, so that electric equilibrium may be produced.

The intensity of a machine may therefore be measured by the quantity of electricity which it can give to a sphere of unit radius.

(*l.*) Suppose two thin concentric conducting shells, of radii  $R$ ,  $r$ , separated by air, the outer in connection with the ground, and therefore at zero of potential; the inner charged with a quantity  $Q$  of electricity. This will be uniformly distributed over its *outer* surface, for a distribution on the inner surface would produce a resultant electric force at points in the substance of the shell: which the second of Newton's results above shows could not be balanced by the external uniformly electrified shells.

Now there must be no resultant electric force at any point of the substance of the outer shell. That this may be the case we must have a quantity  $Q'$  uniformly distributed on its inner surface, such that

$$Q + Q' = 0,$$

$$\text{or} \quad Q' = -Q.$$

Hence also there is no electricity on the outer surface of the outer shell. For a layer  $q$  on the outer surface would produce the potential

$$\frac{q}{r}$$

in the exterior coating which is connected with the earth.

The potential at any point whatever within the outer shell is therefore

$$-\frac{Q}{r}$$

so far as it depends upon  $-Q$ . Hence it is

$$\frac{Q}{R} - \frac{Q}{r}$$

in the substance of the inner shell.

(*m.*) If this arrangement, which is virtually a spherical

jar, be fully charged by connecting with its inner coating a machine which produces a potential  $V$ , while its outer coating is connected with the earth, we must, therefore, have

$$V = \frac{Q}{R} - \frac{Q}{r}.$$

If, as is usually the case,  $R$  and  $r$  are nearly equal—let us put  $r = R + t$ , where  $t$  is the thickness of the shell of air: then

$$V = Q \left( \frac{1}{R} - \frac{1}{R+t} \right) = \frac{Qt}{R^2} \text{ nearly.}$$

If  $S$  be the surface of one of the shells, we have

$$S = 4\pi R^2, \text{ so that } V = 4\pi \frac{Qt}{S}.$$

[We may also obtain this important result as follows:— $2\pi\rho$  = attraction of infinite plate. *Between* two such parallel plates, whose potentials are  $V$  and  $V_0$ , and whose surface densities are  $\rho$  and  $\rho_0$ , the attraction  $= 2\pi(\rho - \rho_0) = \frac{V - V_0}{t}$ .

But if  $V_0 = 0$ , there is no force on points *in* second plate,  $\therefore 2\pi(\rho + \rho_0) = 0, \rho_0 = -\rho; \therefore 4\pi\rho = \frac{V}{t}$ . If  $S$  be the common surface,  $4\pi Q = \frac{SV}{t}$ , as above.]

(*n.*) Suppose a number of additional concentric spherical conducting shells, insulated from one another and uncharged, to be interposed between the two already considered, the condition that the force vanishes in the substance of each requires that the inner surface of each be charged by induction with a quantity  $-Q$  and the outer surface with  $+Q$ . Hence, if there be but one, of which  $\rho$  is the inner radius and  $\tau$  the thickness, our equation for the potential of the innermost shell becomes

$$V = \frac{Q}{R} - \frac{Q}{r} - \frac{Q}{\rho} + \frac{Q}{\rho + \tau}$$

$$= \frac{Qt}{R^2} - \frac{Q\tau}{R^2} = \frac{Q(t-\tau)}{R^2} \text{ nearly.}$$

The same formula will therefore apply to any number of such shells—provided  $\tau$  be put for their joint thickness. Hence the effect of such a substitute for the air is virtually to reduce the distance between the coatings of the jar. A similar effect, but to a less degree, would remain if each of these shells were reduced to detached fragments insulated from one another. This may give the student a hint in understanding how, by the polarisation of its particles, one dielectric may differ from another in specific inductive capacity.

(o.) Thus it appears that, whatever be the dielectric, we have for a Leyden jar the formula

$$V = \frac{Qt}{S}$$

where  $t$  is directly as the thickness of the dielectric, and inversely as its specific inductive capacity.

(p.) The potential energy of the charge is to be found by allowing the separated electricities on the coatings to recombine, and reckoning the work gained.

At any time when the charges on the coatings are reduced to  $q$  and  $-q$ , the potential is

$$v = \frac{qt}{S}.$$

But if electricity, to the amount  $dq$ , now pass from the inner to the outer coating, the work gained is

$$v dq,$$

and therefore the whole work, or potential energy of the charge, is

$$\int_0^Q v dq = \frac{t}{S} \int_0^Q q dq$$

or

$$W = \frac{1}{2} \frac{Q^2 t}{S} = \frac{1}{2} QV.$$

The principle here made use of is easily applicable to the

proof of Helmholtz' general proposition (§ 111), but it requires a rather higher analysis than we have employed in this work.

(*q.*) These simple formulæ enable us to solve many important questions on the subject.

For instance, since

$$Q = \frac{SV}{t},$$

we have

$$W = \frac{1}{2} \frac{SV^2}{t},$$

showing how the potential energy of a fully charged jar depends upon the extent of coated surface, the virtual thickness of the dielectric, and the intensity of the machine employed.

(*r.*) Again, suppose a charge to be divided between two equal jars, by connecting the interior coatings, and also the exterior coatings, of a charged and an empty jar.

At first we have, as before,

$$V = \frac{Qt}{S}.$$

After division, we have  $\frac{Q}{2}$  in each jar, so that the potential falls to half its value.

The work which is stored up is changed from

$$\frac{1}{2} \frac{SV^2}{t} \text{ to } 2 \times \frac{1}{2} \frac{S}{t} \frac{V^2}{4}$$

and is also reduced to half. But, as the conservation of energy requires, the apparently lost half of the original potential energy is expended either mainly in a spark between the inner coatings of the full and empty jars; or, if a conductor of great resistance has been introduced between them, directly in the production of heat. This consideration shows what a large amount of the energy contained in a charged jar is usually wasted in the form of a spark when conductors of small resistance are employed to discharge it.

NOTE C (§ 119).

The potential at any point  $x, y, z$ , due to a magnetic pole of  $m$  units placed at the origin, is

$$\frac{m}{r},$$

where

$$r = \sqrt{x^2 + y^2 + z^2}.$$

If the pole be moved through a small space  $\frac{l}{2}$  in a line whose direction-cosines are  $\lambda, \mu, \nu$ , the expression for the potential at  $x, y, z$  becomes

$$\frac{m}{r} - \frac{ml}{2} \left( \lambda \frac{d}{dx} + \mu \frac{d}{dy} + \nu \frac{d}{dz} \right) \frac{1}{r}.$$

Hence another pole of  $-m$  units, situated at the point whose co-ordinates are  $-\frac{l}{2}\lambda, -\frac{l}{2}\mu, -\frac{l}{2}\nu$ , produces at  $x, y, z$  the potential

$$-\frac{m}{r} - \frac{ml}{2} \left( \lambda \frac{d}{dx} + \mu \frac{d}{dy} + \nu \frac{d}{dz} \right) \frac{1}{r}.$$

From these expressions we see that a small magnet of length  $l$ , which has  $m$  units of magnetism at each pole whose middle point is at the origin, and whose direction-cosines are  $\lambda, \mu, \nu$ , produces at  $x, y, z$  the potential

$$-ml \left( \lambda \frac{d}{dx} + \mu \frac{d}{dy} + \nu \frac{d}{dz} \right) \frac{1}{r}.$$

Hence if we now call  $x, y, z$  the co-ordinates of the middle point of the first small magnet, and if at  $x', y', z'$  another small magnet be placed, having a length  $l'$ , poles of  $m'$  units, and direction-cosines  $\lambda', \mu', \nu'$ , the mutual potential energy of the two magnets is

$$mm'l'l' \left( \lambda \frac{d}{dx} + \mu \frac{d}{dy} + \nu \frac{d}{dz} \right) \left( \lambda' \frac{d}{dx'} + \mu' \frac{d}{dy'} + \nu' \frac{d}{dz'} \right) \frac{1}{r},$$

where  $r$  is now to be treated as

$$\sqrt{(x-x')^2 + (y-y')^2 + (z-z')^2}.$$

From this expression for elementary magnets we may, by the usual processes of sextuple integration obtain at once the expression for the mutual potential energy of any two magnetised masses of steel in the form given by Thomson (*Phil. Trans.* 1852).

It is easy to derive from it, by the principles of energy, the position of equilibrium of either of the magnets (supposed free to turn about its middle point) when the other is fixed in a given position.

We may also easily form the equations of motion of one magnet about its middle point when the other is made to move in a given manner; or when both are started with any initial motions about their middle points and then left to influence each other. Such questions form an interesting and useful exercise for the student.

#### NOTE D (§§ 120-122).

The following is a version of an extract from Helmholtz *Ueber die Erhaltung der Kraft* (1847).

When a magnet moves under the influence of a current, the kinetic energy which it thereby acquires must be derived from the consumption of the energy in the circuit. This consists, during the time  $dt$ , of  $IE dt$  units of heat, or  $JIEdt$  units of work,  $I$  being the intensity of the current, and  $E$  the electromotive force in the circuit. Of this the portion  $JP^2 R dt$ , where  $R$  is the resistance of the circuit, is developed as heat in the conductor (by Joule's law § 139). That acquired by the magnet is

$$I \frac{dV}{dt} dt$$

if  $V$  represent the potential energy of the magnet with reference to unit current in the circuit. We have, therefore,

$$JIE dt = JI^2 R dt + I \frac{dV}{dt} dt$$

whence we obtain

$$I = \frac{E - \frac{1}{J} \frac{dV}{dt}}{R}$$

We recognise in the quantity  $\frac{1}{J} \frac{dV}{dt}$  a new electromotive force, that of the induced current. It always works in a direction opposite to that which would set the magnet in motion in the direction in which it is moving, or would increase its velocity. Since this electromotive force is independent of the intensity of the current, it must remain the same if there were originally no current in the conductor.

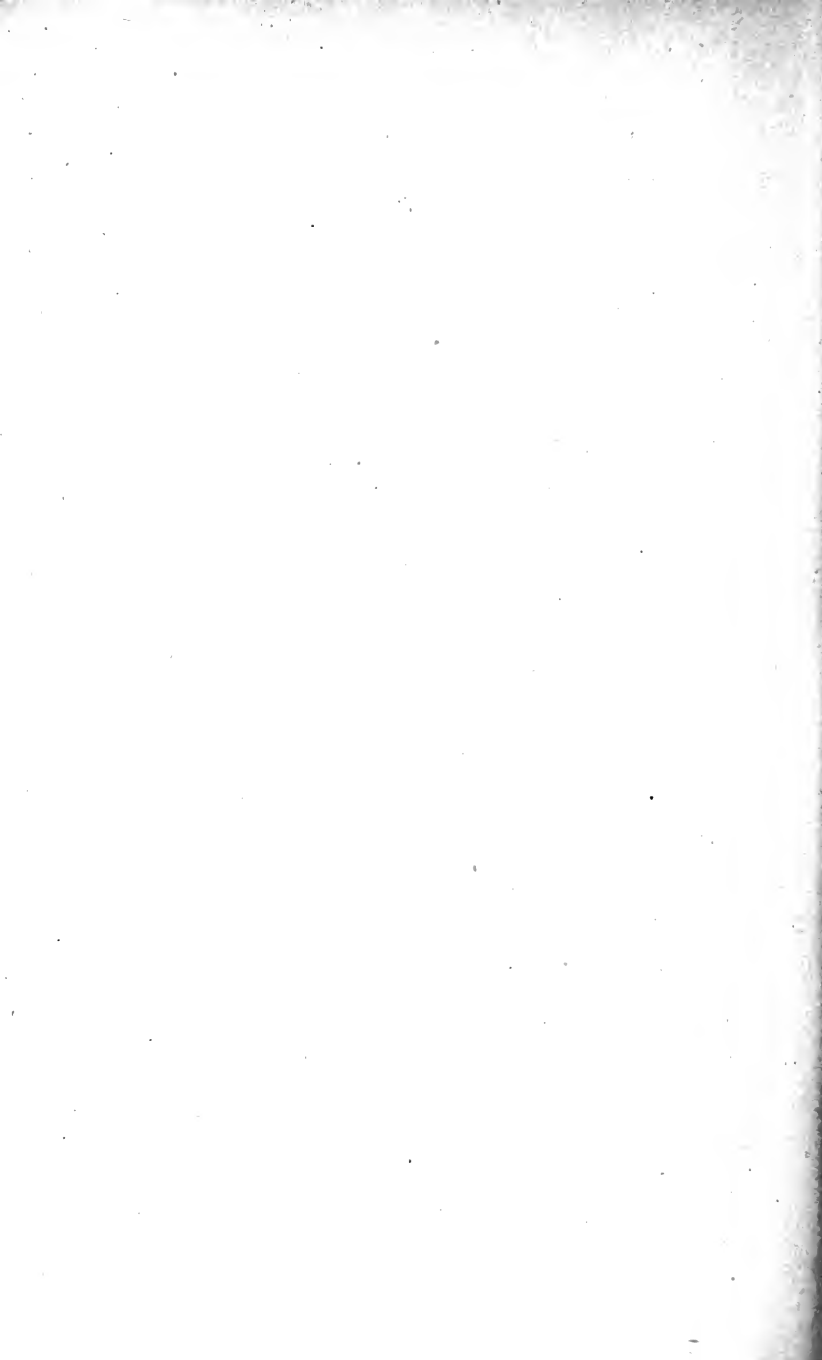
If its intensity vary, the complete current induced during a given time is

$$\int I dt = -\frac{1}{JR} \int \frac{dV}{dt} dt = -\frac{1}{J} \frac{V_i - V_f}{R}$$

where  $V_i$  denotes the initial, and  $V_f$  the final, value of  $V$ . If the magnet be brought up from a great distance

$$\int I dt = -\frac{V_f}{JR}$$

and is independent of the path and of the velocity of the magnet.





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### ERRATA.

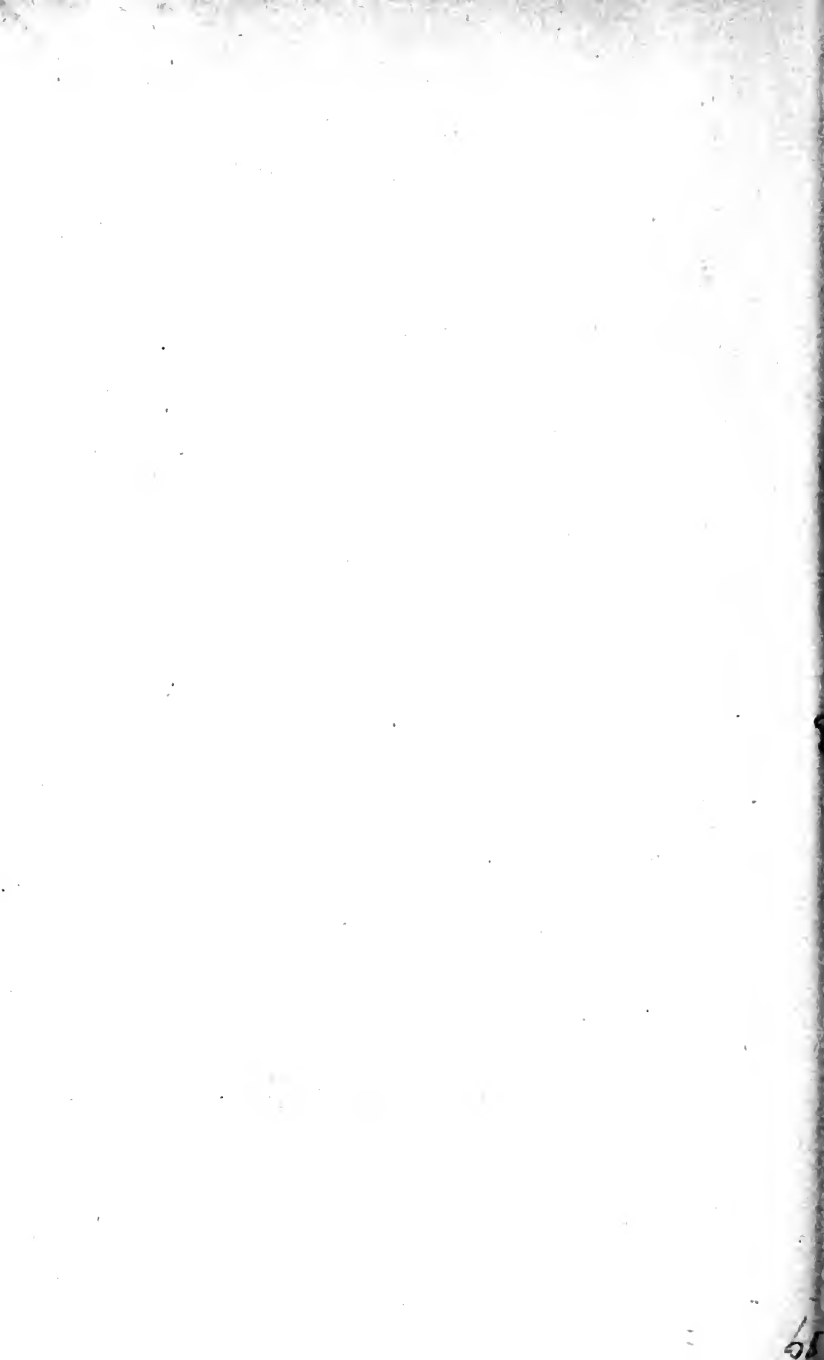
- P. 24, footnote, *for* centrigrade *read* centigrade.
- P. 92, lines 3 and 7, *for* Holtzmann *read* Boltzmann.

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